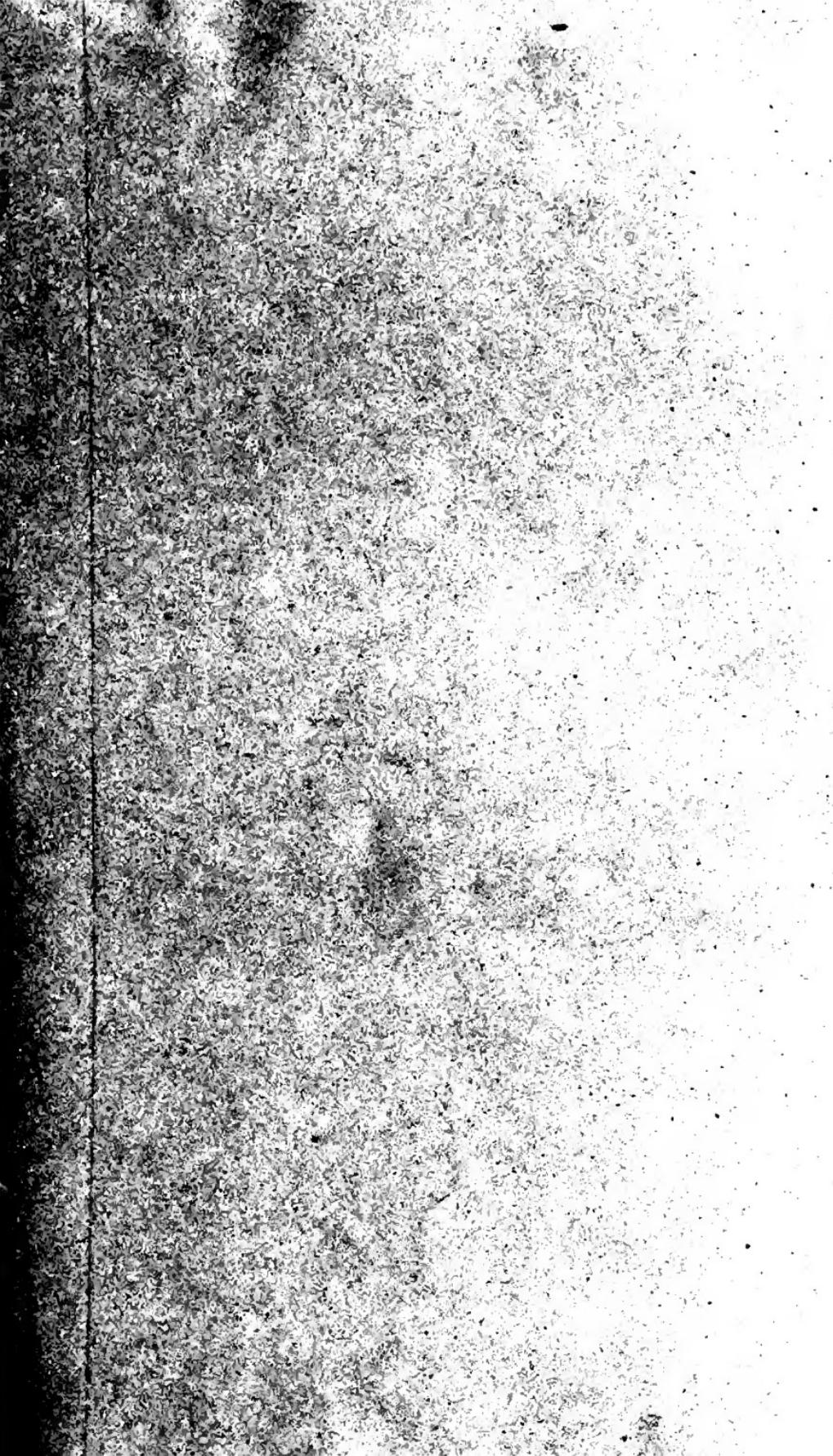


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THE  
LONDON, EDINBURGH, AND DUBLIN  
**PHILOSOPHICAL MAGAZINE**  
AND  
**JOURNAL OF SCIENCE.**

CONDUCTED BY  
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---

"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster  
vilius quia ex alienis libamus ut apes." *Just. Lips. Polit. lib. i. cap. 1. Not.*

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VOL. XXXI.  
NEW AND UNITED SERIES OF THE PHILOSOPHICAL MAGAZINE,  
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JULY—DECEMBER, 1847.

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“Meditationis est perscrutari occulta; contemplationis est admirari perspicua . . . . Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem.”—*Hugo de S. Victore.*



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(THIRD SERIES.)

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- III. Illustrative of Sir D. Brewster's Paper on the Existence of Crystals with different primitive forms and physical properties in the Cavities of Minerals.

*Erratum* in Mr. SYLVESTER's paper, p. 189

Line 14, for  $D'xyz$  read  $D'uvw$ .

*Errata* in Sir GRAVES C. HAUGHTON's paper, vol. xxx. p. 437.

- P. 445, in the thirteenth line from the bottom, *for* 1.1024 *read* 1,1024.  
 — — ninth line from the bottom, *for*  $256^\circ$  *read* 256.  
 — 456, in the third line from the bottom, *for* Hare hair *read* Horse hair.  
 — 518, in the thirteenth line from the bottom, *for* oxide of hydrogen *read* protoxide of hydrogen.  
 — 522, in the fifteenth line from the top, *for* in fault *read* at fault.

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[THIRD SERIES.]

*JULY 1847.*

- I. *On the Perturbations of Planets moving in Eccentric and Inclined Orbits.* By Sir J. LUBBOCK, Bart., F.R.S.\*

THE accuracy of the tables which give for an indefinite time the places of the older planets, is at present sufficient for the purposes of astronomy, and is commensurate with the accuracy of observation; or if this statement appears to be exaggerated, it will at least be admitted that the sensible errors which remain are owing rather to inadvertence in the numerical computation than to the imperfection of the method itself. Such a result is owing to the uninterrupted labours of the greatest mathematicians from the time of Newton, and is justly regarded as one of the greatest triumphs of human intelligence. But it must be recollected that these methods, by which the perturbations of the older planets have been obtained, are applicable only to the case of orbits nearly circular, and little inclined to each other; so that the general solution of the problem of the three bodies, as it is called, remains to the present day imperfect. The methods in use for the older planets are founded, as is well known, upon the development of the disturbing function in terms of the mean anomalies. M. Binet has indeed carried this development to quantities of the seventh order inclusive; but such a development is quite insufficient in the case of comets or planets moving in highly eccentric and inclined orbits, which problem presents far greater difficulty; while the nature of the expression is such, that it is evidently impracticable to carry further such a mode of development, even if the expressions were sufficiently convergent when the eccentricity passes a certain limit.

The only memoir with which I am acquainted which pro-

\* Communicated by the Author.

fesses to give a general solution of the problem otherwise than by mechanical quadratures, is due to M. Hansen. This important work is translated in the *Conn. des Temps* for 1847. That great mathematician has considered the case when  $r < r'$ , that is, when the disturbed body is inferior; and has illustrated the question by the numerical calculation of the perturbations of the comet of Encke by Saturn. M. Hansen develops the disturbing function according to multiple angles of the eccentric anomaly of the disturbed planet *literally*; and first, according to multiple angles of the true anomaly of the disturbing planet; M. Hansen next converts the cosines and sines of the multiple angles of the true anomaly of the disturbing planet into sines and cosines of multiple angles of the mean anomaly of that planet; so that finally the disturbing function is exhibited in terms of the eccentric anomaly of the disturbed planet and the mean anomaly of the disturbing planet; but those series which serve to give the sines and cosines of the multiples of the true anomaly, in terms of sines and cosines of the mean anomaly, are not very convergent; and the process becomes extremely laborious, even in the case which M. Hansen has considered, in which, in consequence of the great distance of Saturn, the approximation does not require to be carried nearly so far as in the case of the perturbations of the same comet by Jupiter, and in many others which may require consideration. Moreover, in this as in every other mode which can be devised of developing the disturbing function *literally*, all quantities must be retained of a given order; although when they are of a different sign, in many instances they destroy each other; but such reductions cannot be foreseen. The numerical substitutions are also extremely laborious, in consequence of the multitude of terms which have to be considered.

As the disturbing function, and others which require to be integrated, are finally exhibited by M. Hansen in terms of two variables, such that direct integration is impossible, M. Hansen has recourse to the integration *par parties*, in which each term by integration gives rise to a series of other terms, the nature of which is complicated.

The method which I propose differs from that suggested by M. Hansen in every particular. Instead of attempting a *literal* development, I insert the numerical values of the elliptic constants in the earliest possible stage: by this means the radical, which expresses the mutual distance of the planets, is explicitly a function of sines and cosines of various angles with numerical coefficients. When  $r < r'$ , I develop in terms of the eccentric anomaly of  $m$ , after having obtained expres-

sions for the co-ordinates of  $m'$  in terms of the eccentric anomaly of  $m$ . Such expressions are very easy to obtain, and are very convergent. It will be recollect that before I endeavoured to develop the disturbing function in the lunar theory in terms of the mean motions of the sun and moon, the invariable practice had been (see *Mécanique Céleste*, vol. iii. p. 189) to express the co-ordinates of the sum in terms of the true longitude of the moon; but the equation which connects the eccentric anomalies of two bodies is far simpler than that which connects the true anomalies, or  $v'$  and  $v$ , and therefore the conversion which I employ is made with greater facility. The quantity under the radical sign in  $R$  may thus be considered as a function, of which the general term can be represented by

$$a \frac{\sin \left( iv + i' \frac{n'}{n} v \right)}{\cos},$$

$a$  being a numerical quantity. The development of this quantity to the power  $-\frac{1}{2}$  or  $-\frac{3}{2}$ , may be facilitated by the use of tables, which give the numerical coefficients in the development of  $\{1 - A \cos \alpha\}^{-\frac{1}{2}}$ ,  $\{1 - A \cos \alpha\}^{-\frac{3}{2}}$ , &c. Such tables have been calculated for me by Mr. Farley. By proceeding in this way, no term is ever introduced which affects the final result beyond a given place of decimals. For the development of the radical admits of being exhibited in the form

$$A + B + C + D + \&c.;$$

such that

$$B = \alpha A \mathbb{Q}, \quad C = \beta B \mathbb{Q}, \quad D = \gamma C \mathbb{Q},$$

so that each term is deducible from the one which precedes it, by the multiplication of that term by  $\alpha \mathbb{Q}$ ,  $\beta \mathbb{Q}$ , &c.,  $\alpha$ ,  $\beta$ ,  $\gamma$ , &c. being proper fractions. If therefore the terms in the two quantities which form those products, such, for instance, as

$$\alpha A \text{ and } \mathbb{Q}$$

which form  $B$ , are sorted and arranged in the order of their numerical magnitude, as soon as any one partial product sinks below any limit that may be assigned, all the succeeding terms are necessarily of inferior magnitude; and the approximation stops, as it were, of itself, without any exercise of thought on the part of the computer.

When  $r > r'$ , that is, when the planet disturbed is superior to the disturbing planet, I am not able to suggest any other course than to develop in terms of the true anomaly of the disturbed planet, and the mean anomaly of the disturbing planet,

and to integrate *par parties*. I have obtained the law of the coefficients in the series which results in this process, and they are highly convergent. I am confident that, by the processes which I have attempted thus so briefly to describe, the perturbations of planets moving in orbits, however eccentric and inclined, may be calculated with nearly as great facility as they are given by existing methods, in orbits nearly circular and in the same plane, and may be exhibited in tables, giving their values for an indefinite period, if required. If these methods, which I have described in detail elsewhere, possess the advantages which I ascribe to them, I hope the time is not distant when the perturbations of Pallas and of some of the comets may be reduced to a tabular form; but as the labour will be very considerable, it will be necessary to limit the inquiry in the commencement to the cases of the greatest emergency.

Although my methods are specially adapted to the determination of the perturbations of bodies moving in eccentric orbits which cannot be developed in terms of the mean motions, yet they embrace also the case of a planet moving in an orbit nearly circular; and it is easy to show in what manner the labour is increased by the greater eccentricity. If the reciprocal of the radical which expresses the mutual distance of the planets be called

$$\frac{\eta}{r^l} \{1 + P\}^{-\frac{1}{2}}, \quad \eta = \frac{a}{\sqrt{a^2 + a'^2}},$$

the chief difficulty arises in developing  $\{1 + P\}^{-\frac{3}{2}}$ . If the numerical values of the elliptic constants are introduced,

$$1 + P = 1 - A_1 \cos \alpha_1 - A_2 \cos \alpha_2 + &c.,$$

$A_1, A_2, \&c.$  are numerical coefficients, which I here suppose ranged in the order of their numerical magnitude. I make

$$\{1 - A_1 \cos \alpha_1\} \{1 - A_2 \cos \alpha_2\} \dots \{1 - A_i \cos \alpha_i\} = 1 + P + Q,$$

including a limited number of terms in  $1 + P + Q$ .

$$\{1 - A_1 \cos \alpha_1\}^{-\frac{3}{2}}, \quad \{1 - A_2 \cos \alpha_2\}^{-\frac{3}{2}} \dots \&c.,$$

can be obtained at once by means of a table. But as the coefficients given by such a table do not readily furnish, by interpolation, the values required unless it be considerably extended, I take for  $A_1, A_2, \&c.$  the nearest value given by the table, and I leave the residue to form part of  $Q$ . In this way it will generally be found sufficient to include not more than six terms in  $1 + P + Q$ , so as to leave  $Q$  consisting of

terms of which the coefficients are each below .1 in numerical value, and the quantity  $\{1+P\}^{-\frac{3}{2}}$  can be developed according to powers of  $Q$  in a rapidly converging series.

$$1+P=1-\frac{2\eta^2}{\sigma}\frac{a'}{r'}\frac{r}{a}\cos\delta+\eta^2\rho.$$

$\frac{2\eta^2}{\sigma}=\frac{2aa'}{(a^2+a'^2)}$ ,  $\delta$  is the angle included by lines drawn from the sun to  $m$  and  $m'$ ,  $\rho=\frac{a'^2r^2}{r'^2a^2}-1$ .

The terms contained in  $\frac{2\eta^2}{\sigma}\frac{a'}{r'}\frac{r}{a}\cos\delta$  obviously exceed greatly in magnitude those contained in  $\eta^2\rho$ ,

$$\frac{r}{a}\cos\delta=i\cos f'+k\sin f';$$

$f'$  being the true anomaly of  $m'$ , and  $v$  the eccentric anomaly of  $m$ ,

$$i=-e\mathfrak{A}+\mathfrak{A}\cos v-\sqrt{1-e^2}\mathfrak{B}\sin v,$$

$$k=-e\mathfrak{C}+\mathfrak{C}\cos v+\sqrt{1-e^2}\mathfrak{D}\sin v;$$

$\mathfrak{A}$ ,  $\mathfrak{B}$ ,  $\mathfrak{C}$  and  $\mathfrak{D}$  being constants, each necessarily less than unity, which depend only on the inclination of the orbits and the position of their line of intersection, and such that when they are in the same plane

$$\mathfrak{A}=\mathfrak{D} \text{ and } \mathfrak{B}=\mathfrak{C}.$$

The process is precisely the same in substance, whether the orbit of  $m$  is highly eccentric and inclined, or circular, and in the same plane with that of  $m'$ ; the only difference being that, while in the former case it may be necessary to detach as many as six terms to form the quantity  $1+P+Q$ , in order that  $Q$  may not contain any term of which the numerical coefficient exceeds .1 in magnitude; in the latter case, supposing  $e'$  the eccentricity of  $m'$  to be inconsiderable,  $1+P+Q$  will only contain one factor, and therefore  $\{1+P+Q\}^{-\frac{3}{2}}$ , &c. can be calculated with greater facility. Thus, for example, in the perturbations of

Pallas by Saturn, it is convenient that  $1+P+Q$  should contain three terms.

Pallas by Jupiter, it is convenient that  $1+P+Q$  should contain four terms.

Encke's comet by Saturn, it is convenient that  $1+P+Q$  should contain five terms.

Encke's comet by Jupiter, it is convenient that  $1+P+Q$  should contain six terms.

And then in each of these examples  $Q$  will contain no term of which the coefficient exceeds .1 in numerical amount.

If

$$\frac{Q}{1+P+Q} = Q,$$

$$\{1+P\}^{-\frac{3}{2}} = A + B + C + D,$$

$$A = (1+P+Q)^{-\frac{3}{2}}, \quad B = \frac{3}{2} Q A, \quad C = \frac{5}{4} Q B,$$

$$D = \frac{7}{6} Q C, \quad E = \frac{9}{8} Q D, \text{ &c.}$$

The calculation of  $\{1+P+Q\}^{-1}$  is much facilitated by the use of a table which gives the values of the coefficients of

$$\{1 - A \cos \alpha\}^{-1}.$$

$\frac{\eta}{r'}$  and  $1+P$  contain terms multiplied by  $\frac{a'}{r'} \cos f'$ ,  $\frac{a'}{r'} \sin f'$ ,  $\frac{a'}{r'}$ , and  $\frac{a'^2}{r'^2}$ , and none others require consideration. If the eccentricity of  $m'$  is small, they may be developed in terms of  $\xi'$ , the mean anomaly of  $m'$ ; and it will be sufficient to consider the terms depending on

$$\cos \xi', \cos 2\xi', \cos 3\xi', \sin \xi', \sin 2\xi', \sin 3\xi'.$$

If  $t$  is the time reckoned from the time of the perihelion passage of  $m$ ,  $r < r'$ ,

$$nt = v - e \sin v;$$

and if  $360^\circ - n'c'$  is the mean anomaly of  $m'$  at the time of the perihelion passage of  $m$ ,

$$\xi' = n't - n'c';$$

and if

$$\frac{n'}{n} v - n'c' = \mathfrak{n},$$

$$\cos i\xi' = \cos i \left\{ \mathfrak{n} - \frac{n'}{n} e \sin v \right\},$$

$$\sin i\xi' = \sin i \left\{ \mathfrak{n} - \frac{n'}{n} e \sin v \right\};$$

and as  $\frac{n'}{n}$  is a fraction,  $\cos i\xi'$  and  $\sin i\xi'$  can be developed in a series rapidly converging, and containing explicitly only the variable quantity  $v$ .

[To be continued.]

II. *On the Discovery of Gun-Cotton.*  
By Professor SCHÖENBEIN\*.

THE substance to which I have given in German the name of *schiesswolle*, and in English that of gun-cotton, having excited a lively curiosity, it may be interesting to the scientific world to become acquainted with some details of the way in which I was first led to its discovery.

The results of my researches on ozone led me in the course of the last two years to turn my attention particularly to the oxides of nitrogen, and principally to nitric acid. The numerous experiments I have made on this subject have led me, as I have stated in detail in Poggendorff's *Annalen*, to adopt a peculiar hypothesis on the so-called hydrates of nitric acid, sulphuric acid, &c., as well as on the normal nitrates, sulphates, &c.

For a long time I had entertained doubts as to the existence of compound bodies of this nature, which cannot be isolated, and which are stated to be capable of existing only in combination with certain other substances; for a long time also I had come to the notion that the introduction of these imaginary combinations had only been an apparent progress in theoretical chemistry, and that it had even impeded its development.

It is well known that what has most contributed to the admission of the existence of these compounds has been the opinion generally received among chemists respecting the nature of nitric acid. Starting from the existence of the compound of nitrogen  $\text{NO}_5$ , as an undoubted and demonstrated fact, notwithstanding the impossibility of isolating it, they always cite nitric acid to prove the existence of compounds which cannot exist in an isolated state. In my opinion, there is no degree of oxidation which is represented by  $\text{NO}_5$ , and what these chemists designate by the formula  $\text{NO}_5 + \text{HO}$  must be considered as being really  $\text{NO}_4 + \text{HO}_2$ ; I am even inclined to regard the normal nitrates  $\text{NO}_5 + \text{RO}$ , as compounds which must be expressed by  $\text{NO}_4 + \text{RO}_2$ . Amongst other motives which induce me to admit this opinion, I will mention the fact that we can obtain hydrated nitric acid or a normal nitrate by the direct mixture of  $\text{NO}_4$  with  $\text{HO}_2$  or  $\text{RO}_2$ . Other considerations, which I have had occasion to detail elsewhere, induce me also to consider hydrated sulphuric acid to have the form  $\text{SO}_2 + \text{HO}_2$ , and not that of  $\text{SO}_3 + \text{HO}$ , and a normal sulphate that of  $\text{SO}_2 + \text{RO}_2$ . It is sufficient here to observe that  $\text{SO}_2$  placed in presence of  $\text{HO}_2$  gives rise to what is

\* From the *Archives des Sciences Physiques et Naturelles*.

called hydrated sulphuric acid, and that  $\text{SO}_2$  placed in presence of  $\text{BaO}_2$  or  $\text{PbO}_2$  gives rise to what is called sulphate of the oxide of barium or of lead. Rose's compound, to which the formula  $2\text{SO}_3 + \text{NO}_2$  has been assigned, should have, in my opinion,  $2\text{SO}_2 + \text{NO}_4$ . Admitting this, I considered it probable that the mixture of  $2(\text{SO}_2 + \text{HO}_2)$  ( $= 2(\text{SO}_3 + \text{HO})$ ) with  $\text{NO}_4 + \text{HO}_2$  ( $= \text{NO}_5 + \text{HO}$ ) yields  $2\text{SO}_2 + \text{NO}_4$ , and that at the same time  $3\text{HO}_2$  is disengaged, or enters into a loose combination with what is called the bisulphate of deutoxide of nitrogen. In other words, I conjectured that a mixture formed with the hydrates of nitric acid and sulphuric acid would possess a very great power of oxidation, and would form a kind of *aqua regia*, in which the combination  $\text{HO}_2$  would act the part of the chlorine. On this hypothesis, and abstracting  $\text{HO}_2$  from the acid mixture by means of a proper oxidable body, there ought to remain Rose's compound.

Guided by these suppositions, which, I admit, may be as little founded as they are contrary to the ideas received among chemists, I commenced in December 1845 a series of experiments with a view to put my hypothesis to the proof: it will be seen in the sequel whether the results at which I arrived tend to confirm it.

I mixed some flowers of sulphur and a certain quantity of the acid mixture of which I have spoken: immediately, even at the temperature of  $32^\circ \text{ F}.$ , a lively disengagement of sulphurous acid gas took place without the production of deutoxide of nitrogen. After the reaction, which was accompanied by a development of heat, there remained a colourless liquid, which, mixed with water, disengaged a considerable quantity of deutoxide of nitrogen, and acted generally as a solution of Rose's compound in hydrated sulphuric acid would have done.

I should add here, that a mixture of four ounces of hydrated sulphuric acid with a single drop of nitric acid, on the addition of flowers of sulphur, disengages a sensible quantity of sulphurous acid. To assure himself of the presence of the latter, the operator has only to hold over the liquid a strip of paper which has been covered with iodide of potassium paste, and tinged slightly blue by exposure to chlorine. The liberated sulphurous acid will soon dissipate this blue colour.

Selenium and phosphorus are oxidized in the same manner at low temperatures in the acid mixture in question; and this latter is modified to such an extent, that, on the addition of water, an abundant disengagement of deutoxide of nitrogen gas takes place.

Iodine even, in the state of powder and shaken up with the

acid mixture, rapidly absorbs oxygen, when exposed to a low temperature; and there is formed, besides iodic acid, the compounds to which Millon has lately drawn attention. After the reaction a liquid remains, which, diluted with water, gives an abundant disengagement of deutoxide of nitrogen and liberates iodine.

My experiments on ozone having shown that this body, which I consider to be a distinct peroxide of hydrogen, forms, as well as chlorine, at the ordinary temperature, a peculiar compound with olefiant gas, without apparently oxidizing in the least either the hydrogen or the carbon of this gas, I had the idea that it would not be impossible that certain organic matters, exposed to a low temperature, would likewise form compounds, either with the peroxide of hydrogen alone, which, on my hypothesis, occurs in a state of combination or of mixture in the acid mixture, or with  $\text{NO}_4$ . It was this conjecture, doubtless very singular in the eyes of chemists, which principally led me to commence experiments with common sugar.

I made a mixture of one part (volume) of nitric acid, of 1·5 spec. grav., and two parts of sulphuric acid of 1·85, at the temperature of 36° F.; I then added some finely powdered sugar, so as to form a very fluid paste. I stirred the whole, and, at the end of a few minutes, the saccharine substance formed itself into a viscous mass entirely separated from the acid liquid, without any disengagement of gas. This pasty mass was washed with boiling water, until this last no longer exercised any acid reaction; after which I deprived it, as much as possible, at a low temperature, of the water it still contained. The substance now possessed the following properties:—Exposed to a low temperature, it is compact and brittle; at a moderate temperature, it may be moulded like jalap resin, which gives it a beautiful silky lustre. It is semi-fluid at the temperature of boiling water; at a higher temperature, it gives off red vapours; heated still more, it suddenly deflagrates with violence, without leaving any perceptible residue. It is almost insipid and colourless, transparent like the resins, almost insoluble in water, but easily soluble in the essential oils, in æther and concentrated nitric acid, and in most cases it acts in general like the resins in a chemical and physical point of view: thus friction renders it very electro-negative. I will add, that the acid mixture, by means of which this resinous body was obtained, has an extremely marked bitter taste.

I wished to make experiments also with other organic substances; and I soon discovered, one after another, all those about which there has been so much said of late, especially in the Academy of Paris. All this passed in December 1845,

and the first few months in 1846. In March, I sent specimens of my new compounds to some of my friends, in particular to Messrs. Faraday, Herschel and Grove. It is necessary to note expressly that the gun-cotton formed part of these products; but I must add, that hardly was it discovered when I employed it in experiments of shooting, the success of which encouraged me to continue them. Accepting the obliging invitation which I received, I went in the middle of April to Wurtemburg, and made experiments with gun-cotton both in the arsenal of Ludwigsburg, in the presence of artillery officers, and in Stuttgart, before the king himself. In the course of May, June and July, with the kind cooperation of the Commandant de Mechel, of M. Burkhardt, captain of artillery, and other officers, I subsequently made in this city (Bâle) numerous experiments with arms of small calibre, such as pistols, carbines, &c., and afterwards with mortars and cannon,—experiments at which Baron de Krüdener, the Russian ambassador, was several times present. I may be allowed to mention, that I was the person who fired the first cannon loaded with gun-cotton and shot, on the 28th of July, if I remember aright, after we had previously ascertained, by experiments with mortars, that the substance in question was capable of being used with pieces of large calibre.

About the same time, and indeed previously, I employed gun-cotton to blast some rocks at Istein in the Grand Duchy of Baden, and to blow up some old walls at Bâle; and in both cases I had opportunities of convincing myself in the most satisfactory manner, of the superiority of this new explosive substance over common gunpowder\*.

Experiments of this kind, which took place frequently and in the presence of a great number of persons, could not long remain unknown; and the public journals soon gave, without participation on my part, descriptions, more or less accurate, of the results which I had obtained. This circumstance, joined to the short notice which I inserted in the May number of Poggendorff's *Annalen*, could not fail to attract the attention of German chemists: in the middle of August I received from M. Böttger, Professor at Frankfort, the news that he had succeeded in preparing gun-cotton and other substances. Our two names thus became associated in the discovery of the substance in question. To M. Böttger the gun-cotton must have been particularly interesting, as he had previously discovered an organic acid which deflagrates readily.

In the month of August I went to England, where, assisted

\* In the month of June I made also the first capsules, and employed them with success for muskets, in the presence of the above-named officers.

by the able engineer, Mr. Richard Taylor of Falmouth, I made numerous experiments in the mines of Cornwall, which were entirely successful, in the opinion of all competent witnesses. Experiments on the action of gun-cotton were also made in several parts of England, under my direction, both with small fire-arms and with pieces of artillery, and the results obtained were very satisfactory.

Until that time there had been little or nothing said of gun-cotton in France; and it will appear that the short notices which Mr. Grove gave at Southampton at the meeting of the British Association, and the experiments with which he accompanied them, served first to attract the attention of French chemists to this substance. At Paris, the thing was at first considered hardly credible, and jokes even were passed upon it; but when there could no longer remain any doubt as to the reality of the discovery, and when several chemists in Germany and other countries had published the processes which they employed to prepare the gun-cotton, then a lively interest was manifested in a subject which had just before excited derision, and it was soon pretended that the new explosive substance was an old French discovery. It was declared to be nothing more than the xyloïdine first discovered by M. Braconnot, and afterwards investigated anew by M. Pelouze, and the only merit left me was to have conceived the happy idea of putting this substance into a gun-barrel. The knowledge of the composition of xyloïdine ought to have sufficed to convince those who put forward that opinion, that it is not suited for fire-arms, on account of its containing too much carbon and too little oxygen for the chief part to be converted into gaseous matters during the combustion. It was moreover very easy to discover the essential differences which exist between the xyloïdine of Braconnot and gun-cotton. Nevertheless the error was kept up for some months.

Matters stood thus, when, on the 4th of last November, a Scotch chemist, Mr. Walter Crum of Glasgow, published a memoir, in which he showed that gun-cotton is not the same product as xyloïdine, but that it presents an essentially different composition; and towards the end of the same month, the French Academy received a communication of the same nature. The gun-cotton was then no longer xyloïdine, it was called pyroxyloïdine, and the first was admitted to be unsuitable for fire-arms.

If, therefore, it is proved that from the commencement of 1846 I prepared gun-cotton, and applied it to the discharge of fire-arms, and that M. Boettger did the same in the month of August,—if it be admitted that xyloïdine cannot serve the

same purposes as this cotton, and if it be notoriously known that what is now called pyroxyloïdine was not brought before the French Academy and the scientific world until towards the middle of last November, the idea of attributing to France the discovery of gun-cotton cannot be seriously entertained, or of assigning to me merely a practical application of that which another would have discovered.

I appeal to the justice of Frenchmen, to decide the point to whom belongs the honour of not only being the first to apply the new substance in question, but also of having first prepared it—to MM. Braconnot and Pelouze, or myself. I must, moreover, add expressly, that it was not xyloidine even which led to my discovery, however intimate may be its relation with gun-cotton ; it was theoretical ideas, possibly very erroneous ones, but which are peculiarly my own, as well as some facts which I was also the first to discover. *Suum cuique* is a principle of morality on which society at large rests ; why should it not be strictly respected in the republic of science ? M. Pelouze is a distinguished chemist, and already possesses a sufficiently high reputation not to require to elevate his pretensions on the merits of others ; and I am fully persuaded that this estimable chemist, of well-known truth of character, will, appreciating with impartiality the circumstances which have occurred, freely render me the justice to which I consider myself entitled.

Bâle, Dec. 28, 1846.

### III. *On the Inverse Calculus of Definite Integrals.* By the Rev. BRICE BRONWIN\*.

THIS paper contains several very simple and easy methods in the inverse calculus of definite integrals ; and they show that the function under the sign of integration may have more than one form. The exponents  $n$  and  $p$  are always positive, and  $n+p=i$  an integer.

First, let  $\varphi(x) = \sum A_m x^m$ , an ascending series. Then

$$\begin{aligned} \int_0^a x^{n-1} dx \varphi(a-x) &= \sum A_m \int_0^a x^{n-1} dx (a-x)^m \\ &= \sum A_m a^{m+n} \int_0^1 x^{n-1} dx (1-x)^m \\ &= \Gamma(n) \sum A_m a^{m+n} \frac{\Gamma(m+1)}{\Gamma(m+n+1)} = \psi(a) \text{ suppose.} \end{aligned}$$

\* Communicated by the Author.

Then also

$$\Gamma(n) \sum A_m (a-x)^{m+n} \frac{\Gamma(m+1)}{\Gamma(m+n+1)} = \psi(a-x);$$

and

$$\begin{aligned} \Gamma(n) \sum A_m \frac{\Gamma(m+1)}{\Gamma(m+n+1)} \int_0^a x^{p-1} dx (a-x)^{m+n} \\ = \int_0^a x^{p-1} dx \psi(a-x), \end{aligned}$$

or

$$\Gamma(n) \Gamma(p) \sum A_m a^{m+i} \frac{\Gamma(m+1)}{\Gamma(m+i+1)} = \int_0^a x^{p-1} dx \psi(a-x).$$

Operate with  $\left(\frac{d}{da}\right)^i$  on both members, and we have

$$\begin{aligned} \Gamma(n) \Gamma(p) \sum A_m a^m &= \Gamma(n) \Gamma(p) \varphi(a) = \left(\frac{d}{da}\right)^i \int_0^a x^{p-1} dx \psi(a-x) \\ &= \left(\frac{d}{da}\right)^i a^p \int_0^1 dv (1-v)^{p-1} \psi(av), \end{aligned}$$

by making  $a-x=av$ . Therefore

$$\left. \begin{aligned} \int_0^a x^{n-1} dx \varphi(a-x) &= \psi(a), \quad \varphi(a) = \frac{1}{\Gamma(n) \Gamma(p)} \\ \left(\frac{d}{da}\right)^i a^p \int_0^1 dv (1-v)^{p-1} \psi(av). \end{aligned} \right\} \dots \quad (1.)$$

Next, let  $\varphi(x) = \sum \frac{A_m}{x^m}$ , a descending series. Then

$$\varphi(a+x) = \sum \frac{A_m}{(a+x)^m},$$

and

$$\int_0^\infty x^{n-1} dx \varphi(a+x) = \sum A_m \int_0^\infty \frac{x^{n-1} dx}{(a+x)^m}$$

$$= \sum \frac{A_m}{a^{m-n}} \int_0^\infty \frac{x^{n-1} dx}{(1+x)^m} = \Gamma(n) \sum \frac{A_m}{a^{m-n}} \frac{\Gamma(m-n)}{\Gamma(m)} = \psi(a)$$

suppose. Therefore

$$\Gamma(n) \sum \frac{A_m}{(a+x)^{m-n}} \frac{\Gamma(m-n)}{\Gamma(m)} = \psi(a+x);$$

and

$$\Gamma(n) \sum A_m \frac{\Gamma(m-n)}{\Gamma(m)} \int_0^\infty \frac{x^{p-1} dx}{(a+x)^{m-n}} = \int_0^\infty x^{p-1} dx \psi(a+x);$$

or

$$\Gamma(n) \Gamma(p) \sum \frac{A_m}{a^{m-i}} \frac{\Gamma(m-i)}{\Gamma(m)} = \int_0^\infty x^{p-1} dx \psi(a+x).$$

Operate with  $\left(\frac{d}{da}\right)^i$  on both members; then

$$(-1)^i \Gamma(n) \Gamma(p) \sum \frac{A_m}{a^m} = \left(\frac{d}{da}\right)^i \int_0^\infty x^{p-1} dx \psi(a+x);$$

or

$$\left. \begin{aligned} \varphi(a) &= \frac{(-1)^i}{\Gamma(n)\Gamma(p)} \left( \frac{d}{da} \right)^i \int_0^\infty x^{p-1} dx \psi(a+x), \\ \int_0^\infty x^{n-1} dx \varphi(a+x) &= \psi(a). \end{aligned} \right\} \quad . . . \quad (2.)$$

We may put  $\varphi(a)$  under a different form by making  $a+x = \frac{a}{v}$ . The forms of  $\varphi(a)$  obtained in (1.) and (2.) differ from those given by Mr. Boole in the Cambridge Mathematical Journal, No. 20; but by varying the process a little, we might obtain his results. We may observe that the least value of  $m$  in (1.) must be greater than  $(-1)$ , and in (2.) greater than  $n+p$  or  $i$ .

In  $\varphi(x) = \epsilon^{xD} \varphi(0)$ , which is Taylor's theorem ( $D$  standing for  $\frac{d}{dx}$ ), change  $\varphi(x)$  into  $\varphi(\epsilon^x)$ , and then  $x$  into  $\log x$ ; we have

$$\varphi(x) + x^D \varphi(\epsilon^0). \quad . . . . . \quad (a.)$$

Therefore, also,

$$\varphi(a-x) = (a-x)^D \varphi(\epsilon^0),$$

and

$$\begin{aligned} \int_0^a x^{n-1} dx \varphi(a-x) &= \left\{ \int_0^a x^{n-1} dx (a-x)^D \right\} \varphi(\epsilon^0) \\ &= \frac{\Gamma(n)\Gamma(D+1)}{\Gamma(D+n+1)} a^{D+n} \varphi(\epsilon^0) = \psi(a). \end{aligned}$$

Consequently

$$\frac{\Gamma(n)\Gamma(D+1)}{\Gamma(D+n+1)} (a-x)^{D+n} \varphi(\epsilon^0) = \psi(a-x),$$

and

$$\begin{aligned} \frac{\Gamma(n)\Gamma(D+1)}{\Gamma(D+n+1)} \left\{ \int_0^a x^{p-1} dx (a-x)^{D+n} \right\} \varphi(\epsilon^0) \\ = \int_0^a x^{p-1} dx \psi(a-x); \end{aligned}$$

or

$$\Gamma(n)\Gamma(p) \frac{\Gamma(D+1)}{\Gamma(D+i+1)} a^{D+i} \varphi(\epsilon^0) = \int_0^a x^{p-1} dx \psi(a-x).$$

Operating with  $\left(\frac{d}{da}\right)^i$  on both members, we find

$\Gamma(n)\Gamma(p)a^D\varphi(\varepsilon^0)=\Gamma(n)\Gamma(p)\varphi(a)=\left(\frac{d}{da}\right)^i \int_0^a x^{p-1} da \psi(a-x),$   
the same result as in (1.).

In (a.) change  $\varphi(x)$  into  $\varphi\left(\frac{1}{x}\right)$ , and then  $x$  into  $\frac{1}{x}$ ; we have

$$\varphi(x)=x^{-D}\varphi(\varepsilon^{-0}); \dots \dots \dots \quad (b.)$$

and therefore

$$\varphi(a+x)=(a+x)^{-D}\varphi(\varepsilon^{-0}),$$

and

$$\begin{aligned} \int_0^\infty x^{n-1} dx \varphi(a+x) &= \left\{ \int_0^\infty x^{n-1} dx (a+x)^{-D} \right\} \varphi(\varepsilon^{-0}) \\ &= \frac{\Gamma(n)\Gamma(D-n)}{\Gamma(D)} a^{n-D} \varphi(\varepsilon^{-0}) = \psi(a). \end{aligned}$$

Hence

$$\frac{\Gamma(n)\Gamma(D-n)}{\Gamma(D)} (a+x)^{n-D} \varphi(\varepsilon^{-0}) = \psi(a+x),$$

and

$$\begin{aligned} \frac{\Gamma(n)\Gamma(D-n)}{\Gamma(D)} \left\{ \int_0^\infty x^{p-1} dx (a+x)^{n-D} \right\} \varphi(\varepsilon^{-0}) \\ = \int_0^\infty x^{p-1} dx \psi(a+x); \end{aligned}$$

or

$$\Gamma(n)\Gamma(p) \frac{\Gamma(D-i)}{\Gamma(D)} a^{i-D} \varphi(\varepsilon^{-0}) = \int_0^\infty x^{p-1} dx \psi(a+x).$$

And, as before,

$$\begin{aligned} (-1)^i \Gamma(n)\Gamma(p) a^{-D} \varphi(\varepsilon^{-0}) &= (-1)^i \Gamma(n)\Gamma(p) \varphi(a) \\ &= \left(\frac{d}{da}\right)^i \int_0^\infty x^{p-1} dx \psi(a+x), \end{aligned}$$

the same result as in (2.).

We might by this method derive the forms of  $\varphi(a)$  given by Mr. Boole; but my object is merely to show one use out of many which may be made of the formulæ (a.) and (b.)

If  $\Delta r=1$ , and  $E=1+\Delta$ ;  $E^k r=r+k$ ,  $E^k x^r=x^r x^k$ . Giving to  $k$  an infinity of different values, multiplying the results by any constants, and taking the sum, we have

$$x^r \varphi(x) = \varphi(E)x^r. \dots \dots \dots \quad (c.)$$

It is plain that we may give to  $k$ , not only integer values, but fractional ones also, and any values whatever, and negative as well as positive ones; for the operation  $E^k$  performed on  $r$ , or on  $x^r$ , merely changes them into  $r+k$ , and  $x^{r+k}$  respectively. The function  $\varphi(x)$  is therefore very general.

Change  $x$  into  $a-x$ , and we have

$$(a-x)^r \varphi(a-x) = \varphi(E)(a-x)^r.$$

Therefore

$$\begin{aligned} & \int_0^a x^{n-1} dx (a-x)^r \varphi(a-x) = \varphi(E) \int_0^a x^{n-1} dx (a-x)^r \\ &= \varphi(E) a^{r+n} \int_0^1 x^{n-1} dx (1-x)^r = \Gamma(n) \varphi(E) a^{r+n} \frac{\Gamma(r+1)}{\Gamma(r+n+1)} = \psi(a) \end{aligned}$$

suppose. Change  $a$  into  $a-x$ , and we have

$$\Gamma(n) \varphi(E)(a-x)^{r+n} \frac{\Gamma(r+1)}{\Gamma(r+n+1)} = \psi(a-x),$$

and

$$\Gamma(n) \varphi(E) \frac{\Gamma(r+1)}{\Gamma(r+n+1)} \int_0^a x^{p-1} dx (a-x)^{r+n} = \int_0^a x^{p-1} dx \psi(a-x);$$

or

$$\Gamma(n) \Gamma(p) \varphi(E) a^{r+i} \frac{\Gamma(r+1)}{\Gamma(r+i+1)} = \int_0^a x^{p-1} dx \psi(a-x),$$

and

$$\Gamma(n) \Gamma(p) \varphi(E) a^r = \Gamma(n) \Gamma(p) a^r \varphi(a) = \left( \frac{d}{da} \right)^i \int_0^a x^{p-1} dx \psi(a-x).$$

Change  $x^r \varphi(x)$  into  $\varphi(x)$ , and transform the second member; then

$$\begin{aligned} & \int_0^a x^{n-1} dx \varphi(a-x) = \psi(a), \quad \varphi(a) = \frac{1}{\Gamma(n) \Gamma(p)} \left( \frac{d}{da} \right)^i a^p \int_a^1 dv \\ & \quad (1-v)^{p-1} \psi(av), \end{aligned}$$

as before.

Resuming the equation

$$\Gamma(n) \varphi(E)(a-x)^{r+n} \frac{\Gamma(r+1)}{\Gamma(r+n+1)} = \psi(a-x),$$

we have

$$\Gamma(n) \varphi(E) \frac{\Gamma(r+1)}{\Gamma(r+n+1)} \int_0^a x^{p-1} dx (a-x)^{r-p} = \int_0^a \frac{x^{p-1} dx}{(a-x)^i} \psi(a-x);$$

or

$$\begin{aligned} & \Gamma(n) \Gamma(p) \varphi(E) a^r \frac{\Gamma(r-p+1)}{\Gamma(r+n+1)} = \int_0^a \frac{x^{p-1} dx}{(a-x)^i} \psi(a-x) \\ &= a^{p-i} \int_0^1 v^{-i} dv (1-v)^{p-1} \psi(av). \end{aligned}$$

Multiply by  $a^{i-p} = a^n$ , and operate with  $\left( \frac{d}{da} \right)^i$ ; there results

$$\Gamma(n) \Gamma(p) \varphi(E) a^{r-p} = \left( \frac{d}{da} \right)^i \int_0^1 v^{-i} dv (1-v)^{p-1} \psi(av).$$

If therefore we change  $x^r \varphi(x)$  into  $\varphi(x)$ , we now have

$$\left. \begin{aligned} \int_0^a x^{n-1} dx \varphi(a-x) &= \psi(a), \quad \varphi(a) = \frac{a^p}{\Gamma(n)\Gamma(p)} \left( \frac{d}{da} \right)^i \\ &\quad \int_0^1 v^{-i} dv (1-v)^{p-1} \psi(av). \end{aligned} \right\} \quad . . . \quad (3.)$$

If we put D for  $\frac{d}{dr}$ , then

$$D^k \epsilon^{rx} = x^k \epsilon^{rx}, \quad (-D)^k \epsilon^{-rx} = x^k \epsilon^{-rx};$$

and, as in (c.), we have

$$\epsilon^{rx} \varphi(x) = \varphi(D) \epsilon^{rx}, \quad \epsilon^{-rx} \varphi(x) = \varphi(-D) \epsilon^{-rx}. \quad . . . \quad (d.)$$

Or, if we put  $\rho^k$  for the operation which converts  $\epsilon^{rx}$  into  $x^k \epsilon^{rx}$ , and  $\theta^k$  for that which changes  $\epsilon^{-rx}$  into  $x^k \epsilon^{-rx}$ , then

$$\epsilon^{rx} \varphi(x) = \varphi(\rho) \epsilon^{rx}, \quad \epsilon^{-rx} \varphi(x) = \varphi(\theta) \epsilon^{-rx}; \quad . . . \quad (e.)$$

and  $k$  may be positive or negative, integer or fractional, or any quantity whatever. I believe these formulæ are new, and they admit of many uses.

Changing  $x$  into  $a+x$ , we have

$$\epsilon^{-r(a+x)} \varphi(a+x) = \varphi(\theta) \epsilon^{-r(a+x)};$$

and

$$\begin{aligned} \int_0^\infty x^{n-1} dx \epsilon^{-r(a+x)} \varphi(a+x) &= \varphi(\theta) \epsilon^{-ra} \int_0^\infty x^{n-1} dx \epsilon^{-rx} \\ &= \Gamma(n) \varphi(\theta) \frac{1}{r^n} \epsilon^{-ra} = \psi(a) \text{ suppose.} \end{aligned}$$

Changing  $a$  into  $a+x$ , this gives

$$\Gamma(n) \varphi(\theta) \frac{1}{r^n} \epsilon^{-r(a+x)} = \psi(a+x),$$

and

$$\begin{aligned} \Gamma(n) \varphi(\theta) \frac{1}{r^n} \epsilon^{-ra} \int_0^\infty x^{p-1} dx \epsilon^{-rx} &= \Gamma(n) \Gamma(p) \varphi(\theta) \frac{1}{r^p} \epsilon^{-ra} \\ &= \int_0^\infty x^{p-1} dx \psi(a+x); \end{aligned}$$

or

$$\begin{aligned} (-1)^i \Gamma(n) \Gamma(p) \varphi(\theta) \epsilon^{-ra} &= (-1)^i \Gamma(n) \Gamma(p) \epsilon^{-ra} \varphi(a) \\ &= \left( \frac{d}{da} \right)^i \int_0^\infty x^{p-1} dx \psi(a+x). \end{aligned}$$

Change the function  $\epsilon^{-rx} \varphi(x)$  into  $\varphi(x)$ , and we have

$$\begin{aligned} \int_0^\infty x^{n-1} dx \varphi(a+x) &= \psi(a), \quad \varphi(a) = \frac{(-1)^i}{\Gamma(n)\Gamma(p)} \left( \frac{d}{da} \right)^i \\ &\quad \int_0^\infty x^{p-1} dx \psi(a+x) \end{aligned}$$

as heretofore.

The equation

$$\Gamma(n)\varphi(\theta) \frac{1}{r^n} \varepsilon^{-ra} = \psi(a),$$

found in this investigation, gives

$$\Gamma(n)\varphi(\theta) \frac{1}{r^n} \varepsilon^{-r} \left( \frac{a}{v} \right) = \psi \left( \frac{a}{v} \right),$$

and

$$\begin{aligned} \Gamma(n)\varphi(\theta) \frac{1}{r^n} \int_0^1 v^{-p} dv (1-v)^{p-1} \varepsilon^{-r} \left( \frac{a}{v} \right) &= \int_0^1 v^{-p} dv \\ &\quad (1-v)^{p-1} \psi \left( \frac{a}{v} \right). \end{aligned}$$

Differentiate this for  $a$ , then

$$\begin{aligned} -\Gamma(n)\varphi(\theta) \frac{1}{r^{n-1}} \int_0^1 v^{-p-1} dv (1-v)^{p-1} \varepsilon^{-r} \left( \frac{a}{v} \right) &= \frac{d}{da} \int_0^1 v^{-p} dv \\ &\quad (1-v)^{p-1} \psi \left( \frac{a}{v} \right). \end{aligned}$$

Make  $\frac{1}{v} - 1 = x$ , and

$$\int_0^1 v^{-p-1} dv (1-v)^{p-1} \varepsilon^{-r} \left( \frac{a}{v} \right)$$

will be transformed into

$$\varepsilon^{-ra} \int_0^\infty x^{p-1} dx \varepsilon^{-rax} = \Gamma(p) \frac{a^{-p}}{r^p} \varepsilon^{-ra};$$

and the preceding will become

$$-\Gamma(n)\Gamma(p)\varphi(\theta) \frac{a^{-p}}{r^{i-1}} \varepsilon^{-ra} = \frac{d}{da} \int_0^1 v^{-p} dv (1-v)^{p-1} \psi \left( \frac{a}{v} \right).$$

Multiply by  $a^p$ , and operate with  $\left( \frac{d}{da} \right)^{i-1}$ , there results

$$\begin{aligned} (-1)^i \Gamma(n)\Gamma(p)\varphi(\theta) \varepsilon^{-ra} &= (-1)^i \Gamma(n)\Gamma(p) \varepsilon^{-ra} \varphi(a) \\ &= \left( \frac{d}{da} \right)^{i-1} a^p \frac{d}{da} \int_0^1 v^{-p} dv (1-v)^{p-1} \psi \left( \frac{a}{v} \right). \end{aligned}$$

After changing the function  $\varphi$ , as before, we now have

$$\left. \begin{aligned} \int_0^\infty x^{n-1} dx \varphi(a+x) &= \psi(a), & \varphi(a) &= \frac{(-1)^i}{\Gamma(n)\Gamma(p)} \\ \left( \frac{d}{da} \right)^{i-1} a^p \frac{d}{da} \int_0^1 v^{-p} dv (1-v)^{p-1} \psi \left( \frac{a}{v} \right). \end{aligned} \right\} \quad \dots \quad (4.)$$

The formulæ (3.) and (4.) are the same as those given by Mr. Boole in the paper before referred to. From the last

method of investigation, it appears that the functions  $\phi$  and  $\psi$  may be any whatever, consistent with the required relation between them. But if we are obliged to integrate by series, they will in general be subject to the restrictions mentioned in (1.) and (2.); I say, in general, for infinite quantities may vanish by the operations  $\left(\frac{d}{da}\right)^i$ .

To give an example in each of the theorems: in (1.) let

$$n = \frac{1}{2}, p = \frac{1}{2}, \psi(x) = \sqrt{x}.$$

We find

$$\left\{ \Gamma\left(\frac{1}{2}\right) \right\}^2 \phi(a) = \frac{d}{da} \left( \frac{\pi a}{2} \right),$$

and

$$\phi(a) = \frac{1}{2};$$

then

$$\psi(a) = \sqrt{a},$$

as it should be.

In (2.) let

$$n = \frac{1}{2}, p = \frac{1}{2}, \psi(x) = \frac{1}{\sqrt{x}}$$

We find,

$$\left\{ \Gamma\left(\frac{1}{2}\right) \right\}^2 \phi(a) = \frac{d}{da} (\log a - \log o), \quad \phi(a) = \frac{1}{\pi a};$$

and then

$$\psi(a) = \frac{1}{\sqrt{a}}.$$

In the last example  $n$  and  $p$  are not conformed to the restrictions, but the infinite quantity goes out by differentiation. The theorems (3.) and (4.) are likewise satisfied by these examples. It must not be supposed that the values of  $\phi(a)$ , given in (1.) and (3.), or in (2.) and (4.), are necessarily equal; for they will not reduce the one to the other. Yet we may have

$$\int_0^\infty x^{n-1} dx \phi(a+x) = \psi(a), \quad \int_0^a x^{n-1} dx \phi(a-x) = \psi(a)$$

in both cases; since we know from examples that the integrals of different functions may be of the same form.

Gunthwaite Hall, near Barnsley,  
May 24, 1847.

*IV. On certain Phænomena of Voltaic Ignition and the Decomposition of Water into its constituent Gases by Heat.*  
*By W. R. GROVE, Esq., M.A., F.R.S.\**

**I**N the Philosophical Magazine for August 1841, I recommended for eudiometrical purposes, the use of a platinum wire ignited by a voltaic battery. In fig. 1 is represented a form of apparatus for this purpose; it consists of a tube of Bohemian glass, with a loop of platinum wire  $\frac{1}{80}$ th of an inch diameter sealed into its upper end; the size of the glass tube may be adapted to the quantity of gas sought to be analysed, and may when necessary be reduced to extremely small dimensions, one-eighth of an inch being ample; into this the gas may readily be made to ascend, by the insertion of a wire of copper, platinum, or glass, as may be suitable to the gas: two cells of the nitric-acid battery are sufficient fully to ignite the wire, and the same battery supplies, by electrolysis, pure oxygen and hydrogen for the analysis. Since the period when I first proposed this, I have seldom used any other apparatus for such gaseous analyses as are performed by combining the gas to be examined with oxygen or hydrogen. This eudiometer possesses the advantage of enabling the operator either to detonate or slowly to combine the gases, by using different powers of battery, by interposing resisting wires, or by manipulation alone,—a practised hand being able by changing the intervals of contact to combine or detonate the gas at will. My general practice has been to produce a gentle heat in the wire until the gases contract, and then gradually to increase the heat until a full ignition takes place, by which means all the objects of the eudiometer of Volta are fulfilled, without detonation, without dependence on the fickle electric spark, and without thick tubes, any danger of explosion, or of the gases being projected from the eudiometer.

I have commenced with a description of this eudiometer, as it has been indirectly the means of my undertaking the experiments detailed in this lecture; and as its very great convenience has never been generally understood, I think that in strongly recommending it, I shall be of service to chemists.

In a paper honoured by insertion in the Philosophical Transactions for 1845, p. 358, I have shown another method of eudiometry also performed by voltaic ignition; in that experiment the vapour of camphor was decomposed into carbonic oxide and carburetted hydrogen; it was an application



\* From the Philosophical Transactions for 1847, part i.; having been received by the Royal Society September 3, and read November 19, 1846.

of voltaic ignition to effects analogous to those produced by Priestley and others, by passing compound gases through ignited tubes of porcelain.

But the voltaic process has this immense advantage, that the heat can be rendered incomparably more intense; that the quantity of vapour or gas to be operated on may be indefinitely small; that there are no joints, stop-cocks or ligatures; and that there is no chance of endosmose, which takes place through all porcelain vessels. I therefore determined to examine by these means several gases, both with a view of verifying, under different circumstances, known results, and seeking for new effects by this new and advantageous application. I used an eudiometer (fig. 1) of 8 inches long and 0·4 inch internal diameter, exposing the gases to intense heat, and subsequently analysed the residues in one of the same length, but 0·2 inch diameter.

I will first consider the physical effects of different gases on the ignition of the wire itself.

In a paper on the Application of Voltaic Ignition to lighting Mines\*, I have mentioned the striking effects of hydrogen in reducing the intensity of ignition of a platinum wire, so much so that a wire voltaically ignited to incandescence in atmospheric air, is apparently extinguished by inverting over it a jar of hydrogen; with other gases the effects are not so striking, and with them these differences are best shown by including a voltameter in the circuit. Davy found that the conducting power of a wire diminished in proportion to the degree to which it was heated: assuming the accuracy of this position, the amount of gas in the voltameter would be inverse to the intensity of ignition in the wire. The following is the result I obtained with different gases, employing the same battery (the nitric-acid combination at its most constant period), the same wire, and the same vessel:—

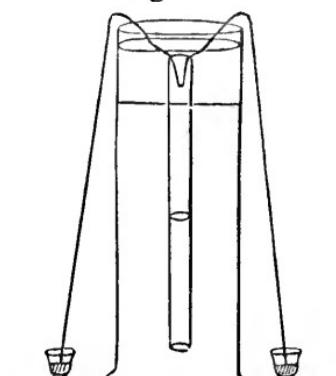
Gases surrounding the wire.	Cubic inches of gas evolved in the voltameter, per minute.
Hydrogen . . . . .	7·7
Olefiant gas . . . . .	7·0
Carbonic oxide . . . . .	6·6
Carbonic acid . . . . .	6·6
Oxygen . . . . .	6·5
Compressed air, 2 atmospheres	6·5
Nitrogen . . . . .	6·4
Atmospheric air . . . . .	6·4
Rarefied air . . . . .	6·3
Chlorine . . . . .	6·1

To ascertain the relation between the amount of radiant heat generated by the same battery and wire in gases which presented striking differences as to the luminous effects of the platinum wire, an apparatus was prepared in which the bulb of a thermometer was retained at a certain distance from the coil of wire ignited by a battery of four cells, and exposed, first, to an atmosphere of hydrogen, and then to one of atmospheric air, at the same temperature and pressure; the thermometer rose  $7\frac{1}{2}^{\circ}$  in five minutes in the hydrogen, and  $15^{\circ}$  in the air in the same time. Both the heating and luminous effects appear therefore to be greater in atmospheric air than in hydrogen. I cannot satisfactorily account for the differences shown in the above table; there appears a general tendency to greater ignition in the electro-negative than in the combustible gases, but the facts are far too few to found a generalization. I was at first inclined to regard the difference of effect in hydrogen as analogous to the peculiarity mentioned by Leslie\* respecting its convection of sound, but the parallel does not hold; sound is transmitted imperfectly through rarefied air, and also through hydrogen; on the contrary, the heat of the ignited wire is most intense in the former, and least so in the latter; the heat is also very much reduced in intensity in the compounds of hydrogen, ammonia and olefiant gas, or even by a small admixture of hydrogen with another gas, such as nitrogen; hydrogen, therefore, appears to have a peculiar and specific action in this respect.

I now pass to the consideration of the effects of the ignited wire on different gases. The ignition was in every case raised to the fullest extent, and the gases after exposure to it were carefully cooled down to their original temperature.

When the experiments were made over water, the whole eudiometer was immersed in a vessel of distilled water, occasionally having an inch depth of oil on the surface (see fig. 2†); when over mercury, and a long-continued exposure was required, a bent tube was employed, as at fig. 3, the closed end being immersed in water or oil, to prevent the fusion of the glass which would otherwise have ensued.

Fig. 2.

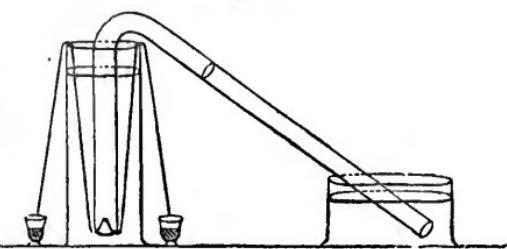


\* Transactions of the Cambridge Philosophical Society, vol. i. p. 267.

† In this and in figs. 3 and 5, the lines leading from the platinum loop to the mercury cups represent copper wires.

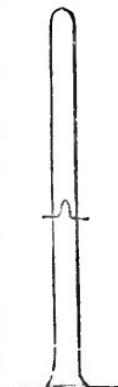
The tubes are much more easily preserved from cracking, and the ignition better kept up with oil on the exterior than with water, but as in many of these experiments I might have been considerably misled by a crack in the glass, or a bad sealing of the wire, allowing a portion of oil to enter the tube, I used water in the greater number of them until I was assured of the phænomena.

Fig. 3.



The apparatus, fig. 3, is superior in one respect to fig. 2, even for experiments over water, as the wire being situate below the volume of gas, the circulation is more rapid. This object may also be effected by employing the form of eudiometer, fig. 4, in which the loop of wire is near the centre of the tube, so as to be just above the surface of water in the tube; there are, however, some difficulties of manipulation with this form, which render it practically of less value than fig. 1.

Fig 4.



*Binoxide of nitrogen* over distilled water contracted differently in proportion to the heat of the wire; in the best experiment it contracted to one-third of its original volume; the residual gas was nitrogen.

Nitric acid was found in solution in the water.

Over mercury the effects were nearly the same; the mercury was attacked, and the orange fumes of nitrous acid were visible.

*Protioxide of nitrogen* was decomposed into nitrogen and oxygen; the volume increased by 0·35 of the original volume; I could not get the full equivalent proportion, or 0·5 of oxygen.

*Carbonic acid* underwent no perceptible alteration.

*Ammonia* increased to double its original volume; it was now no longer absorbable by water, and gave three volumes of hydrogen, plus 1 nitrogen.

*Olefiant gas* contracted slightly, deposited carbon, the residue being hydrogen and olefiant gas, more of the former in proportion to the heat, but I could not succeed in entirely decomposing it.

*Nitrogen* suffered no change.

*Oxygen* gave a very slight contraction, amounting to  $\frac{1}{50}$ th of its volume; the oxygen employed was very pure, obtained from chlorate of potash and manganese, and also from water

by electrolysis : no change in properties was perceptible in the oxygen after its exposure to the ignited wire. This contraction I incline to attribute to a slight portion of hydrogen present, which view will, I think, be considered as strengthened by the effect of the ignited wire on hydrogen, to be presently detailed. I at one time thought that the contraction might be due to a slight oxidation of the wire, but it never went beyond a very limited point; nor was the wire altered in size or weight, though it was kept ignited for many hours.

*Chlorine* over water gave dense white fumes ; a grayish-yellow insoluble powder accumulated on the sides of the tube near the platinum wire, which appeared of the same nature as the vapours ; the deposit was insoluble in cold nitric, sulphuric, or muriatic acid, but dissolved by the last when boiled. The fumes did not, as far as I could judge, affect litmus paper ; a barely perceptible tinge of red was indeed communicated to it, but this, I had every reason to believe, was attributable to a slight portion of muriatic acid not absorbed by the water. I have not yet worked out this result, as it is probable, considering the number of experiments that have been made on heated chlorine, that it is a known product, though I cannot find, in several books to which I have referred, any substance answering to it in description, and the field opened by voltaic ignition is so new that each result demands a separate and prolonged examination ; if I find that this is an unknown compound I shall probably resume its investigation\*.

*Cyanogen* gave, though in very minute quantities, a somewhat similar deposit, but at its then very high temperature it began to act rapidly on the mercury, and I was obliged to give up the experiment after an hour's ignition. Both these gases require peculiar and novel apparatus for examination by voltaic ignition. It will presently be seen that my whole attention and disposable time were necessarily occupied with certain phænomena to which this class of experiments ultimately led me.

*Hydrogen* gave a very notable contraction, amounting in some cases to one-tenth of its volume. This was an unexpected result, and I examined it with care. It took place both over water and over mercury ; rather more with the former than with the latter. It obtained equally with hydrogen procured by electrolysis from carefully distilled water and pure sulphuric acid ; with that procured from common zinc and pure sulphuric acid diluted with distilled water ; and with that obtained from distilled zinc and pure diluted sulphuric acid. The contraction was less when the water from which

\* See Supplemental paper.

the hydrogen was obtained was carefully purged of air by boiling and the air-pump, but yet there was a notable contraction even when the water had been freed from air to the utmost practicable extent. In the numerous experiments which I made on this subject, the contraction varied from the  $\frac{1}{10}$ th to the  $\frac{1}{30}$ th of the whole volume.

After many fruitless experiments I traced it to a small quantity of oxygen which I found hydrogen to contain under all circumstances in which I examined it. Phosphorus placed in hydrogen, obtained with the utmost care, gives fumes of phosphorous acid, shines in the dark and produces a slight contraction, but there is after this a further contraction by the use of the ignited wire.

I may cite the following as an easy experiment and simple illustration of the rapidity with which hydrogen appropriates oxygen. Let hydrogen be collected over water well-purged of air; let a piece of phosphorus remain in it until all combustion has ceased, the hydrogen will then be full of phosphoric vapour; fill another tube with water, and pass the hydrogen rapidly into it, the second tube will instantly be filled with a dense white fume of phosphorous acid; the hydrogen having instantly carried with it oxygen from the stratum of water it has passed.

A very careful experiment was made as follows:—distilled water was boiled for several hours, to this was added one-fortieth part by measure of pure sulphuric acid, and it was cooled under the receiver of an air-pump; it was now placed in two test-glasses, connected by a narrow inverted tube, full of the same liquid: platinum electrodes were placed in each glass, and the hydrogen caused to ascend immediately into the eudiometer tubes; the whole was completed within two or three minutes after the water had been removed from the air-pump. Here the ordinary sources of impurity in hydrogen were avoided; no zinc was used, the sulphuric acid was pure, and the quantity was so small, that, had it not been pure, the error could have been but very trifling. The hydrogen so obtained, contracted in volume  $\frac{1}{26}$ th; hydrogen prepared in the same way, and exposed to phosphorus, gave dense white fumes; the phosphorus was luminous in the dark for more than an hour, and the contraction (temperature and pressure being carefully examined) was  $\frac{1}{90}$ th; the amount of contraction by the wire would of course equal three times the volume of oxygen mixed with the hydrogen, consequently the oxygen would be  $\frac{1}{78}$ th of the whole volume; the platinum wire induces therefore a greater absorption of oxygen than the phosphorus, unless the volume of hydrogen is increased by the phosphoric

vapour; the sequel of this paper will render it probable that even the ignited wire does not and cannot induce combination of all the oxygen existing in the hydrogen.

I have looked into the papers of MM. Berzelius and Dulong, and of M. Dumas on the equivalent weight of hydrogen. The latter contains a most careful experimental investigation, and is by far the best determination we have; although it is not there mentioned that hydrogen contains oxygen, yet a correction is made for the air contained in the sulphuric acid employed. M. Dumas does not state how the quantity of that air is calculated. There can be no question that nothing approaching in elaborate care to these experiments has been yet performed on the subject; but with the fullest consciousness of M. Dumas' skill, I have, in all my experiments, perceived such an inveterate tendency of hydrogen to possess itself of oxygen, that I cannot help entertaining some doubts whether we have yet the real weight of hydrogen within the assigned limits of error.

It is difficult to see how hydrogen can be absolutely deprived of oxygen which has once existed in it; neither an oxidable metal as zinc, or an ignited inoxidable metal as platinum, getting rid of all the oxygen, and phosphorus, if it does so, replaces it by its own vapour. The near approach, however, of the equivalent of hydrogen, as determined by M. Dumas, to the ratio of whole numbers, renders it probable that it is a very close approximation to the truth.

I have not been able to detect nitrogen in the hydrogen, but the probability is that a slight quantity also exists in it. Whether the oxygen proceeds from portions of air still remaining in solution in the liquid from which the air is exhausted, or whether it is a part of the water actually decomposed, but of which the oxygen is not absorbed by the zinc, is a question to resolve which further experiments are necessary.

*Hydrogen and carbonic acid* mixed in equal volumes were readily acted on by the ignited wire; they contracted to 0·48 of the original volume; the residue was carbonic oxide; one equivalent of oxygen had therefore united with the hydrogen; and the slight additional contraction was probably due to the further combination of hydrogen with oxygen, as above stated.

*Carbonic oxide* exhibited a remarkable effect, and one which, coupled with the last experiment, gave rise to considerations which mainly led to the results to be detailed in the body of this paper. Carbonic oxide, very pure and carefully freed from carbonic acid, was exposed to the ignited wire over distilled water; the gas increased in volume in one experiment to one-

third of its original volume, in the greater number of instances to one-fifth : this increase depended upon the intensity of ignition, which it was very difficult to maintain at its maximum on account of the frequent fusions of the platinum wires.

Here again I had a long research and many erroneous guesses, which I need not detail. The effect did not take place with perfectly dry gas over mercury, and I thence was led to attribute it to some combination with aqueous vapour ; the increase turned out to be occasioned by the formation of carbonic acid. By agitation with caustic potash or lime water the gas was reduced to exactly its original bulk, but it was now found to be mixed with a volume of hydrogen equal to the volume of carbonic acid by which it had been increased ; it was thus perfectly clear that half a volume or one equivalent of oxygen derived from the vapour of the water, had combined with one volume or equivalent of carbonic oxide, and formed one volume or equivalent of carbonic acid, leaving in place of the carbonic oxide with which it had combined, the one volume or equivalent of hydrogen with which it had been originally associated.

Comparing the last experiment, viz. that of mixed carbonic acid and hydrogen with this, I was naturally struck with the curious reversal of affinities under circumstances so nearly similar ; in the one case, hydrogen taking oxygen from carbonic acid to form water and leaving carbonic oxide ; in the other, carbonic oxide taking oxygen from water to form carbonic acid and leaving hydrogen.

I thought much upon this experiment ; it appeared to me ultimately that the ignited platinum had no specific effect in producing either composition or decomposition of water, but that it simply rendered the chemical equilibrium unstable, and that the gases then restored themselves to a stable equilibrium according to the circumstances in which they were placed with regard to surrounding affinities ; that if the state of mixed oxygen and hydrogen gas were, at a certain temperature, more stable than that of water, ignited platinum would decompose water as it does ammonia.

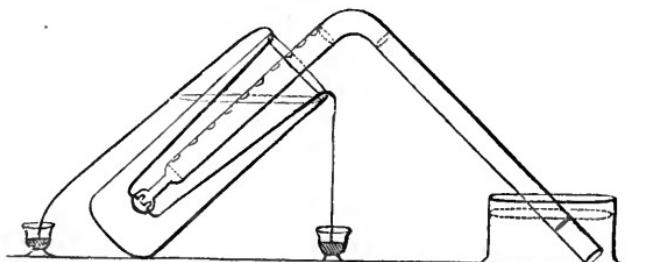
This is a very crude expression of my ideas, but we have no language for such anticipatory notions, and I must adapt existing terms as well as I am able.

It now appeared to me that it was possible to effect the decomposition of water by ignited platinum ; that, supposing the atmosphere of steam in the immediate vicinity of ignited platinum were decomposed, or the affinities of its constituents loosened, if there were any means of suddenly removing this atmosphere I might get the mixed gases ; or secondly, if, as

appeared by the last two experiments, quantity had any influence, that it might be possible so to divide the mixed gases by a quantity of a neutral ingredient as to obtain them by subsequent separation (or as it were filtration) from the neutral substance. Both these ideas were realized.

To effect the first object, after, as usual in such circumstances, much groping in the dark, I cemented a loop of platinum wire in the end of a tube retort similar to fig. 3, and covered it with asbestos, ramming this down so as to form a plug at the closed extremity of the tube, the platinum wire being in the centre. My object was, by igniting the platinum wire, to drain the water out of the asbestos, and the ignited wire being then in an atmosphere of steam, I hoped the water would by capillary attraction keep constantly oozing down to the platinum wire as the steam or decomposed water ascended. The experiment did not succeed; the water established a current through the asbestos by washing away fine particles, and the phenomena of ordinary ebullition took place, unless the intensity of the battery was very much exalted, when a very slight decomposition was perceptible, which I attributed to electrolysis. This experiment, however, suggested another which did succeed. In one or two cases the asbestos plug became compressed above the platinum and so choked up the tube that the wire suddenly fused. It now occurred to me that by narrowing the glass tube above the platinum wire I had the result at my command, as the narrow neck might be made of any diameter and length, so as just to allow the water to drip or run down as the steam forced its way up; a tube was so formed, and is shown with its accompaniments at fig. 5.

Fig. 5.



The result of this experiment was very striking: when two cells of the nitric-acid battery were applied the air was first expanded and expelled, the water then soon boiled, and at a certain period the wire became ignited in the steam. At this instant a tremulous motion was perceptible, and separate bubbles of permanent gas of the size of pin-heads ascended,

and formed a volume in the bend of the tube. It was not a continuous discharge of gas as in electrolysis, but appeared to be a series of rapid jerks; the water, returning through the narrow neck, formed a natural valve which cut off by an intermitting action portions of the atmosphere surrounding the wire; the experiment presented a novel and indescribably curious effect. The gas was oxyhydrogen. It will occur at the first to many of those who hear this paper read, that this effect might be derived from electrolysis. No one seeing it would think so for a moment; and although I shall by my subsequent experiments, I trust, abundantly negative this supposition, yet as this was my first successful experiment on this subject, and is *per se* an interesting and striking method of showing the phænomenon of decomposition by heat, I will mention a few points to prove that the phænomenon could not be occasioned by electrolysis.

To account for it by electrolysis, it must be supposed that the wire offered such a resistance to the current that this divided itself, and the excess of voltaic power passed by the small portion of water which trickled down, instead of by the wire.

In the first place, the experiment was performed with distilled water, and only two cells of the battery employed, which will not perceptibly decompose distilled water.

2ndly. No decomposition took place until the instant of ignition of the wire, though there was a greater surface of boiling water exposed to the wire before than after the period of ignition.

3rdly. A similar experiment was made, but with the wire divided in the centre so as to form two electrodes, and the water boiled by a spirit-lamp; here the current had no wire to conduct any part of it away, but the whole was obliged to pass across the liquid, and yet no decomposition took place, or if there were any it was microscopic.

4thly. When, instead of oil, distilled water was used in the outer vessel\*, even the copper wires, one of which would form an oxidable anode, gave no decomposition across the boiling water outside, while the ignited wire inside was freely yielding mixed gases.

5thly. To prevent the water from being the shortest line for the current, I repeated the experiment with a perfectly straight wire (fig. 6). The result was precisely the same, but the experiment is more difficult; as a certain length of

\* January 8.—I have since found that the exterior tube of oil or water may be dispensed with in this experiment, as the water which trickles down prevents the fusion of the glass.

wire is necessary, the sealing is more troublesome, and the size of the bulb is much more difficult to adapt to the production of steam in exactly the requisite quantity; the straight wire being more suddenly extinguished and more easily fused: with careful manipulation however it succeeds equally well with the former experiment.

I might add other experiments and arguments, but I believe when the remainder of this paper has been read, that the above will be thought scarcely necessary.

I now directed all my efforts to produce the effects by heat alone without the battery. I will mention a few of my unsuccessful attempts, as it will save trouble to future experimenters. I sealed a platinum wire into the extremity of a curved tube, filled the latter with water, and applied a strong heat by the blowpipe to the projecting end of the wire, hoping that the conducting power of the platinum, although inferior to that of most other metals, was sufficiently superior to that of glass to enable me to ignite the portion of the wire within the tube, and thus surround it with an atmosphere of steam; the water however all boiled off from the glass; nor could I succeed in igniting the platinum by heat from without. A similar failure occurred when, on account of its superior conducting power, a gold wire was substituted for that of platinum.

I sealed spongy platinum and bundles of platinum wire into the ends of Bohemian glass tubes, closing the glass over them, and then filling the tubes with water and heating the whole extremity; but the water boiled off from the glass, and the platinum could not be made to attain a full incandescence.

After many similar trials I returned to the battery, and sought to apply it in a manner in which electrolysis could not possibly take place. I had hoped, as I have above stated, to obtain a residual decomposition of water by masking or diluting the gases by a neutral substance. I therefore tried the following experiment: a tube similar to fig. 1 was filled with water which had been carefully freed from air by long boiling and the air-pump; it was then inverted in a vessel of the same water, and a spirit-lamp applied to its closed extremity, until the upper half was filled with va-

Fig. 6.

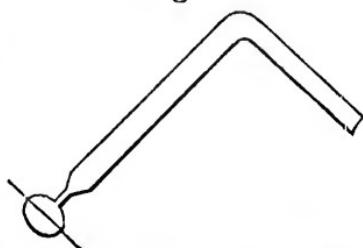
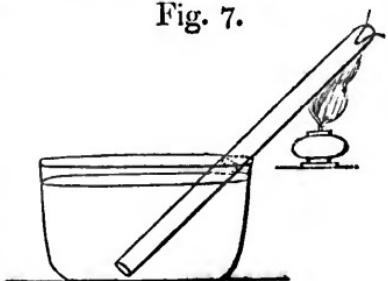


Fig. 7.



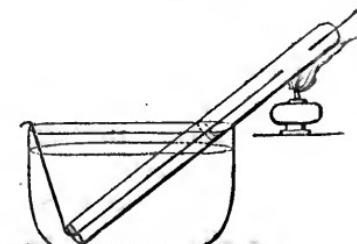
pour (fig. 7). The wire was brought to a full ignition by the battery, and kept ignited for a few seconds; connexion was then broken and the lamp removed, so that the water gradually ascended. A bubble of the size of a large mustard-seed was left in the extremity of the tube, and I was much gratified at finding that when this was caught by a lighted match at the surface of the water-trough it detonated. The experiment was then repeated, continuing the ignition for a longer time, but the gas could not be increased beyond a very limited quantity; indeed it was not to have been expected, as supposing it to be mixed gas, recombination of the excess would have taken place, and the fact of any uncombined gas existing when exposed to incandescent platinum, will doubtless surprise those who hear it for the first time.

The experiment was repeated as at first and the bubble transferred to another tube; the wire was then again ignited in vapour, another bubble was instantly formed and transferred, and so on, until after about ten hours' work sufficient gas was collected for analysis; this gas was now placed in an eudiometer, it detonated and contracted to 0·35 of its original volume; the residue being nitrogen. The experiment was repeated several times with the same general results, the residue sometimes containing a trace of oxygen.

Here electrolysis was out of the question; the wire was ignited in (if I may use the expression) dry steam, the upper part of the tube being far above the boiling-point, and of course perfectly transparent; if not an effect of heat, it must have been a new function of the electric current, at least one hitherto unknown.

As the voltaic arc and electric spark afford heat of the greatest intensity, I tried a succession of electric sparks from platinum wires through steam in the apparatus fig. 8, the water, as in all my experiments, having been previously purged of air (to save circumlocution I will in future call it prepared water). The sparks were taken from the hydro-electric machine of the London Institution; they had in the steam a beautiful crimson appearance; on cooling the tube a bubble was perceptible, which detonated by the match.

Fig. 8.



As in the previous experiments, a whole day's work did not increase the bubble, but when it was transferred another instantly formed; the gas was similarly collected; it detonated

and contracted to 0·4 of its original volume; the residue was nitrogen with a trace of oxygen.

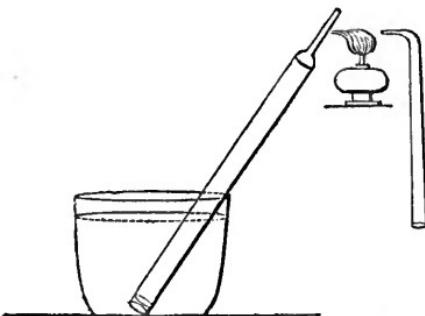
This experiment will again surprise by its novelty; the very means used in every laboratory to combine the mixed gases and form water, here decompose water\*. From a vast number of experiments which I have made on the voltaic and electric disruptive discharges (which are I believe similar phenomena, differing only in quantity and intensity), I believe the decompositions produced by them are the effects of heat alone, and this experiment was therefore to my mind a repetition of the last under different circumstances; others however may think differently. This experiment also I several times repeated.

By counting the globules given off, and comparing a certain number of them with the average volume of steam in the last two experiments, an attempt was made to ascertain what proportion of water could be decomposed by an ignited platinum wire in aqueous vapour, or, which amounts to a corollary from this proposition, what degree of dilution would enable mixed gas to exist without combustion in an atmosphere of steam exposed to an ignited platinum wire. The proportion in an experiment in which the globules were so counted, was 1 to 2400; the probability is however that different temperatures of the platinum wire would give different volumes of gas so decomposed, the volume being greater as the wire is more intensely ignited.

Although there was no known effect of electricity which could produce the phenomenon exhibited by the last two experiments, and it was in any event new, still, firmly convinced that it was an effect of heat, I again determined to attempt its production by heat alone, and without the use of the battery. I procured a tube of silver 9 inches long and 0·4 inch diameter; at the extremity of this was a platinum cap to which a smaller tube, also

Fig. 9.

of platinum, was soldered. This platinum tube was closed at the end and soldered with gold solder. The apparatus was filled with prepared water; the water was boiled in the tube to expel the air from the narrow tube and any which might have adhered to the vessel;



\* I need scarcely point out the distinction, in fact, between this experiment and those in which liquid water has been decomposed by the electric spark. See Supplemental Paper.

the tube was then, when full of hot water, inverted into water, and the flame of a common blowpipe made to play against the platinum tube (fig. 9) until a white heat was obtained. Upon inverting it under water, a bubble of the size of a mustard-seed rose to the surface, which gave a very feeble detonation with the match. Similar bubbles were collected as before, and the gas in an eudiometer contracted to 0·7. On repetition the experiment did not succeed so well, and upon several repetitions it sometimes succeeded and sometimes failed, and I should not mention it but that it was the first experiment which gave me, although not very satisfactorily, the effect of decomposition by heat alone. The reason of its uncertainty I believe to have been the want of a sufficiently intense heat, as I dared not venture on account of the gold solder to push the ignition very far; in fact, I subsequently fused the extremity and spoiled the apparatus by applying the oxyhydrogen flame to it; had the platinum tube been welded instead of gold-soldered, it would doubtless have succeeded better. I should state that the object of the silver tube was to prevent the chance of recombination by the catalytic effect of a large platinum surface; to have, in short, a small portion of platinum exposed to the steam, and that at a high temperature: œconomy was also no indifferent consideration. This experiment, although, coupled with the previous ones, tolerably conclusive, did not satisfy me, and I attacked the difficulty in another manner. The experiment (fig. 5) induced me to believe that if I could get platinum ignited under water so as to be in an atmosphere of steam, decomposition would take place; and M. Boutigny's experiments on the spheroidal state of water led me to hope I might keep platinum for some time under conditions suitable for my purpose.

After a few failures I succeeded perfectly by the following experiment. The extremity of a stout platinum wire was fused into a globule of the size of a peppercorn, by a nitric-acid battery of thirty cells; prepared water was kept simmering by a spirit-lamp, with a tube filled with water inverted in it; charcoal being the negative terminal, the voltaic arc was taken between that and the platinum globule until the latter was at the point of fusion; the circuit was now broken, and the highly incandescent platinum plunged into the prepared water: separate pearly bubbles of gas rose into the tube, presenting a somewhat similar effect to experiment (fig. 5). The process was repeated, the globule being frequently plunged into the water in a state of actual fusion; and when a sufficient quantity of gas was collected it was examined, it detonated,

leaving 0·4 residue; this was as usual nitrogen with a trace of oxygen. A second experiment gave a still better result, the gas contracting to 0·25 of its original volume.

On making the platinum negative and the charcoal positive, a very different result followed: the carbon was, as is known to electricians, projected upon the platinum; and the gas in this case was mixed with carburetted hydrogen and carbonic oxide. I know no experiment which shows so strikingly the different effects at the disruptive terminals as this; when the platinum is negative it gives much carbonic gas, when it is positive, not a trace (the gas was delicately and carefully tested for it); nay, more, by changing the platinum from negative to positive the carbon is instantly removed, and in a single experiment the platinum becomes perfectly clean.

Here then I produced very satisfactorily decomposition by heat; it is true, the battery was used, but used only as a means of fusing the platinum, as this was, as soon as fused, entirely separated from the circuit and could have no possible voltaic action. Wishing however altogether to avoid the use of the battery, I repeated this experiment, employing as my means of fusing the platinum the oxyhydrogen blowpipe; the experiment was equally successful, perhaps more so, as the manipulation was more easy.

I could readily by this means collect half a cubic inch or more of the gas; when detonated, the residue of nitrogen averaged 0·35 of the original volume.

In carefully watching this experiment, I observed that at first a rapid succession of bubbles ascended into the tube from the incandescent platinum, it then became quiescent; the spheroidal state was assumed by the water and no gas ascended; on losing the spheroidal state a sudden hiss was heard, and a single bubble ascended into the tube. I determined to examine separately the gas from the platinum before and after the quiescent state; to effect this I placed two inverted tubes in the capsule with the orifices near each other; the platinum at the point of fusion was immersed under one tube, say tube A, and as soon as the ascent of bubbles ceased, it was removed across to tube B, and the last bubble then entered that tube; the gases from each tube were separately analysed, and tube A gave nearly all detonating gas, the residue being only 0·2; tube B gave none; the gas collected in it was nitrogen, with a trace of oxygen.

In order to examine the effect of an oxidable metal under similar circumstances, I fused by the oxyhydrogen blowpipe the end of a stout iron wire, plunged it into prepared water and collected the globules of gas; no oxygen was given off,

or at least no more than I have always found to accompany hydrogen, which with a small residue of nitrogen was the gas given off in this experiment.

[To be continued.]

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*V. Invention of Fluxions. By CHARLES RICHARD WELD, Esq.*

*To the Editors of the Philosophical Magazine and Journal.*

GENTLEMEN,

**I**N the course of my researches in the archives of the Royal Society, with reference to a history of the Society which I am compiling, I have been much struck with a very remarkable discrepancy on a most important point, connected with the celebrated dispute of the invention of fluxions, between the original Minutes of the Society and the statements of writers on this subject.

Sir David Brewster and Professor De Morgan, following others, state that at a meeting of the Society held on the 20th of May 1714, a resolution was inserted in the Minutes, that "it was never intended that the report of the committee was to pass for a decision of the Society\*." This alludes to the report presented by the committee appointed by the Society to determine the question of the invention of fluxions. Now the exact words of the minute are these:—

"It was not judged proper (since this letter was not directed to them†) for the Society to concern themselves therewith, nor were they desired so to do; but that if any person had any material objection against the Commercium or the report of the committee, it might be reconsidered at any time‡."

There is nothing here to show that the Society *resolved* (and this is the word Mr. De Morgan uses) upon repudiating the report of their committee; so far from this, the opposite conclusion is at once obvious, which is in keeping with the original resolution of the Society *adopting* the report of their Committee, *nemine contradicente*. The point is of great moment; for had the Society come to the resolution as represented, a strong case would be made out against Newton. I have examined the Minutes of the meeting in question with the greatest care, and confidently assert that there is no other allusion to the dispute between Leibnitz and Newton. In conclusion, I wish to state that it is at the request of some of

\* See Life of Newton by Brewster, p. 211, and Life by De Morgan, p. 93.

† Alluding to a letter of Leibnitz to Chamberlayne, complaining of the report of the committee.

‡ Journ. Book, vol. xi. p. 431.

our most eminent philosophers that I send you this "correction," which they conceive ought to be made public through the medium of the Philosophical Journal.

I am, Gentlemen,

Your humble Servant,

Royal Society, Somerset House,  
June 11, 1847.

CHARLES RICHARD WELD.

*VI. Researches on the Composition and Characters of certain Soils and Waters belonging to the Flax districts of Belgium, and on the Chemical Constitution of the Ashes of the Flax Plant. By Sir ROBERT KANE, M.D., M.R.I.A.\**

A BOUT two years since, I had the honour to submit to the Royal Irish Academy the results of some inquiries into the chemical composition of the flax and hemp plants, and into the chemical phænomena of the treatment which they undergo in the preparation of the ligneous fibre for the purposes of the arts. The main object of that memoir was to point out that, whilst the plant, as a whole, was rich in alkalies, earths, sulphuric and phosphoric acids, &c., the fibre, as ultimately purchased in the market, was practically destitute of all these materials, which therefore remained amongst the substances removed from the plants during their preparation, and hitherto rejected as of no use. Those results being published in the Proceedings of the Royal Irish Academy, and copied thence into various agricultural books and journals, have in some degree led to the œconomising of those valuable residues; and it is to be hoped that, according as the attention of farmers becomes more definitely fixed upon the real and philosophical principles of the growth and composition of various crops, the utilization of the different parts of plants will be still more carefully attended to.

The researches to which I have referred, involved the determination of the elementary composition of the plants, only so far as it was necessary to prove the presence and proportional quantity of certain materials in the plant as it grows, and their absence in the fibre as prepared; but it was not my design therein at all to discuss the very important questions, so fundamental to vegetable chemistry and physiology, of the degree within which the composition of the ashes of a plant may vary; or whether there is any general expression within which the constitution of the mineral elements of a plant is necessarily contained; or finally, whether there can be traced

\* Read at the Agricultural Evening Meeting of the Royal Dublin Society, held on the 6th of April 1847.

any positive relation between the composition of the plant and the composition of the soil upon which it grows. To answer these questions even approximatively, will require investigations frequently repeated, and the concurrent labours of many different investigators; and although my present inquiries may serve to furnish certain grounds for arriving at an opinion upon these points, I would not in any way be understood as putting them forward with that view.

My main object, in the inquiry which forms the subject of the present paper, was to ascertain, if possible, whether there existed any difference between the composition of the ashes of the ordinary flax of Ireland and the flax grown in those localities in Belgium, where that plant is known to yield a fibre of so much commercial value. Further, to ascertain the composition of the soils of those districts, in order to compare them with the soils of the localities in Ireland where flax is, or may be, successfully cultivated. Finally, as it is known that in the preparation of the fibre the most important stage consists in the steeping or retting of the plant, I considered it of the greatest interest to trace, if possible, whether the superior qualities of some rivers or ponds in Belgium could be connected with any peculiarity of chemical constitution. For the materials and specimens necessary for these investigations, I am indebted to the kindness and liberality of Mr. Marshall of Leeds; who was anxious also to connect therewith the discussion of some most important points of special technical application, for which, however, the pressure of other avocations did not allow me time. I therefore publish the results contained in the present paper, solely under their scientific relations to agricultural chemistry and physiology, and shall not enter upon any considerations belonging to manufacturing practice.

Before entering into the description of the numerical results of the analyses, I think it better to premise a succinct notice of the modes of analyses adopted for the different classes of substances, as I shall thereby be enabled to avoid a great deal of repetition.

### 1. *Of the Modes of Analyses used for the Ashes, Soils and Waters.*

The preparation of the flax-ashes was effected by chopping up the plant stems into moderately small bits, and then carbonizing them gently in a Hessian crucible. The material so obtained was further incinerated by very gentle ignition in a platinum capsule over a gas flame; but it was not in any way sought to burn off all charcoal, or to obtain the ash perfectly

white, as such would require a temperature capable of materially altering the constitution of the ash, a fact of which I have been long aware, and which has latterly fixed the attention of several chemists.. The ash so prepared was carefully dried in a stove, and then treated in the following manner:—

Dilute muriatic acid having been poured over the quantity of ash selected for analysis, the whole was heated in a water-bath until it dried completely down; water was then added, and when the soluble materials had been completely taken up, the whole was thrown upon a weighed filter and the liquor separated; there remained upon the filter such particles of sand or soil as had been adherent to the plants, the unburned charcoal of the ash, and the silica which had existed in the ash, either free or in combination with alkaline or earthy bases.

The weight of this insoluble residue having been properly determined, it was boiled in a strong solution of caustic potash, by which all the proper silica of the ash was taken up, and the residue then remaining being weighed, gave the sand and charcoal, the silica being thus determined by difference.

The muriatic solution was then divided into three parts for the determination—

1. Of the alkaline constituents.
2. Of the phosphoric acid, manganese, alumina, magnesia, and lime.
3. Of the sulphuric acid and oxide of iron.

The first portion of solution was rendered slightly alkaline by carbonate of ammonia, and then mixed with solution of caustic barytes in excess, and allowed to stand for some hours. By this means the sulphuric and phosphoric acid were perfectly removed, as well as the earthy constituents, except a small quantity of lime, which remained dissolved in a caustic state, and which was then perfectly removed by the addition in excess of a mixture of caustic and carbonated ammonia. The liquor, after filtration, was evaporated to dryness, and the residue gently ignited, when the ammoniacal salts were perfectly expelled: there remained the alkalies of the ash as chlorides. This residue was weighed, then dissolved in water, and a solution of bichloride of platinum added. The liquor and precipitate were then evaporated nearly to dryness, the potash platinum salt washed by a mixture of alcohol and æther, and the amount of platinum determined in the usual way. The soda was ascertained by subtracting the weight of the chloride of potassium from the weight of the mixed chlorides, as given in the first instance.

To the second portion of the liquor was added so much ammonia as nearly neutralized it without producing any per-

manent precipitate. A quantity of perchloride of iron was then added, and acetate of potash, until a deep wine-red colour was produced ; the liquor was then boiled until all odour of acetic acid ceased, and a copious brown precipitate formed, which was separated by the filter. This precipitate was then redissolved in muriatic acid, boiled until all odour of acetic acid ceased, and the liquor then precipitated by ammonia. The precipitate, collected on a filter, was dried, ignited, and weighed, then redissolved by muriatic acid. A quantity of tartaric acid was added to the liquor, and ammonia then added in such excess as to redissolve the precipitate which first forms. To the solution thus got, hydrosulphuret of ammonia was added in excess, the sulphuret of iron collected on a filter, and, when washed, redissolved in aqua regia. The peroxide of iron, precipitated from the liquor by ammonia, collected, dried, ignited and weighed, and its weight subtracted from the weight of the basic phosphate previously given, determines in an absolute manner the quantity of phosphoric acid.

To the liquor from which the phosphoric acid had been separated by the means described above, hydrosulphuret of ammonia was added, by which a precipitate was formed, which was collected, and, while moist, boiled with caustic potash liquor ; the undissolved matter was dissolved in muriatic acid nearly neutralized, and treated with benzoate of ammonia ; by this a trace of iron, generally remaining from the preceding process, was removed, and the manganese was then precipitated by carbonate of ammonia, collected, ignited and weighed. The potash liquor was then acidulated by muriatic acid, and the alumina which it had dissolved was precipitated, and its quantity determined in the usual way.

The solution, from which the iron, alumina, and manganese had thus been separated by hydrosulphuret of ammonia, was next boiled until all odour of sulphuretted hydrogen ceased, and then treated with oxalate of ammonia, the oxalate of lime collected was gently ignited with carbonate of ammonia, and the quantity of lime determined. The liquor was then very much concentrated by evaporation, and treated with phosphate of soda and ammonia, set aside until the ammoniacomagnesian phosphate had perfectly deposited, and the quantity of magnesia determined from that of the latter salt.

The third portion of the ash liquor was treated with nitric acid, so as perfectly to peroxidize the iron ; it was then decomposed by chloride of barium, by which all the sulphuric acid was separated as sulphate of barytes, collected and weighed. To the filtered liquor there was added a great excess of phosphate of soda and ammonia, and then an excess of acetic acid.

By boiling, the whole of the iron separated as perphosphate, and was collected, ignited, and the quantity of oxide of iron calculated from its weight.

For the determination of the chlorine, a totally distinct portion of ash was taken, digested with water, acidulated with nitric acid, and then precipitated with nitrate of silver in the usual way.

It will be observed that, in all its main features, this plan of examination of the ash coincides with that employed by Will and Fresenius, and proposed by them in their memoir on the Composition of certain Ashes. It is, however, that which I had followed in all my former ash analyses, except in regard to the determination of the phosphoric acid, for which I had previously made use of the method proposed by Schulze, but now replaced with so much advantage by that invented by Will.

It is necessary, however, to remark, that the composition of the perphosphate of iron, given by Will, and upon which he founds his mode of determining the quantity of oxide of iron, has been contested very recently by Wittstein, who has not succeeded in preparing that salt with the composition assigned to it by Will. According to the latter chemist, it consists, in its anhydrous form, of  $2\text{Fe}_2\text{O}_3 + 3\text{PO}_5$ , that is,

$2\text{Fe}_2\text{O}_3$	.. . . .	160	42.99
$3\text{PO}_5$	.. . . .	213	57.11
		<hr/> 373	<hr/> 100.00

whilst the salt uniformly obtained by the other chemists was  $\text{Fe}_2\text{O}_3 + \text{PO}_5$ , or

$\text{Fe}_2\text{O}_3$	.. . . .	80	52.98
$\text{PO}_5$	.. . . .	71	47.02
		<hr/> 151	<hr/> 100.00

But the circumstances of preparation of the different salts do not appear to have been quite identical; and I do not, therefore, reject Will's numbers, which have been, moreover, verified by some trials made in my own laboratory. I have consequently employed his formula in calculating the amount of iron in the different materials; but it is easy to calculate, for each analysis, the change (in most cases trifling) which the employment of Wittstein's formula for the perphosphate should introduce.

In the examination of the soils, the process consisted, first, in mechanically separating the sandy and gravelly materials from the finely-divided portion, by careful elutriation with the smallest possible quantity of pure water. This having been

done, and the quantity of sand determined by direct weighing, the finely-divided earthy material was carefully dried at the highest temperature it would bear without its organic constituents being injured, and then weighed. It was then carefully but gently ignited in a current of air, until the organic materials were burned out, and was then again weighed. The loss of weight gave the quantity of organic substance, together, however, with some traces of water, from which the soil could not be previously perfectly freed.

The soil was then subjected, for the determination of its chemical constituents, to precisely the same general plan of treatment which I have described in the case of the ash. The matter, insoluble in muriatic acid, was however found to be (the sand and organic matters having been previously separated) ferruginous clay, which it was not necessary further to examine, as all the materials of importance, in studying the chemical nature of the soil, had been taken up by the different solvents used.

In the case of the waters, the quantity employed for analysis was, with one exception, about two gallons; in that case, owing to a vessel having leaked (No. 3), but one gallon was employed. The waters were, in the first instance, very carefully filtered; and where any sensible quantity of sediment was found upon the filter, its nature and quantity observed.

The water was then evaporated, at first upon the sand-bath, but finally upon a water-bath, to perfect dryness, and the residue having been collected and dried at  $212^{\circ}$ , was weighed. It was then incinerated; the residue, moistened with carbonate of ammonia, again gently ignited and weighed. By the difference of weight, the quantity of organic matter present was ascertained in the state in which it exists when dried at  $212^{\circ}$  Fahrenheit.

The solid material thus obtained was treated with water, until all soluble salts were taken up, and the alkalies, lime, magnesia, with sulphuric and muriatic acids, therein determined. The undissolved residue was next treated with muriatic acid, and the amount and nature of the earthy substances taken up, as well as oxides of iron, &c., and phosphoric acid, if any, ascertained. The material insoluble in muriatic acid, when present, was of course determined.

The detailed modes of analyses pursued in these cases were precisely the same as in those of the ashes and soils.

In carrying out the greater part of the practical details of these analytical methods, I derived valuable aid from Mr. William Sullivan, then my private assistant, but now first chemical assistant in the Museum of Irish Industry, founded by Her Majesty's Government in Dublin.

## 2. Results of the Analyses of the Soils.

The general character of all the soils submitted to examination was that of light, sandy loams, in some cases almost purely sandy; excessively loose in texture, non-coherent and permeable: usually rich in organic matters containing nitrogen. These soils all coloured water boiled upon them, and gave to it a sensible, though very small, quantity of alkaline and earthy salts.

## A. Soil from Heestert, in the Courtrai district:—

	Composition per cent.
Potash . . . . .	0·160
Soda . . . . .	0·298
Peroxide of iron . . . . .	3·298
Oxide of manganese . . . . .	a trace
Alumina . . . . .	2·102
Lime . . . . .	0·357
Magnesia . . . . .	0·202
Sulphuric acid . . . . .	0·025
Phosphoric acid. . . . .	0·121
Chloride of sodium . . . . .	0·017
Organic matter and water not driven off at 212° } . . . . .	3·123
Clay . . . . .	14·920
Sand . . . . .	<u>75·080</u>
	99·703
Loss . . . . .	0·297
	<u>100·000</u>

## B. Soil from Escamaffles, some of the very best flax lands of the Courtrai district:—

	Composition per cent.
Potash . . . . .	0·123
Soda . . . . .	0·146
Peroxide of iron . . . . .	1·663
Oxide of manganese . . . . .	a trace
Alumina . . . . .	1·383
Lime . . . . .	0·227
Magnesia . . . . .	0·153
Sulphuric acid . . . . .	0·017
Phosphoric acid . . . . .	0·152
Chloride of sodium . . . . .	0·030
Organic matter and water not driven off at 212° } . . . . .	2·361
Clay . . . . .	9·280
Sand . . . . .	<u>84·065</u>
	99·600
Loss . . . . .	·400
	<u>100·000</u>

## C. Soil from Hamme Zog, the best flax land in the Antwerp district :—

	Composition per cent.
Potash . . . . .	0·068
Soda . . . . .	0·110
Peroxide of iron . . . . .	1·202
Oxide of manganese . . . . .	a trace
Alumina . . . . .	1·125
Lime . . . . .	0·481
Magnesia . . . . .	0·140
Sulphuric acid . . . . .	0·013
Phosphoric acid . . . . .	0·064
Chloride of sodium . . . . .	0·067
Organic matter and water not expelled at 212° } . . . . .	4·209
Clay . . . . .	5·760
Sand . . . . .	86·797
	<hr/>
	99·975
Loss . . . . .	·025
	<hr/>
	100·000

## D. Soil from a district producing coarse flax and poor crops generally :—

	Composition per cent.
Potash . . . . .	0·151
Soda . . . . .	0·206
Peroxide of iron . . . . .	1·543
Oxide of manganese . . . . .	no trace
Alumina . . . . .	0·988
Lime . . . . .	0·366
Magnesia . . . . .	0·142
Sulphuric acid . . . . .	0·026
Phosphoric acid . . . . .	0·193
Chloride of sodium . . . . .	0·009
Organic matter and water not expelled at 212° } . . . . .	3·672
Clay . . . . .	4·400
Sand . . . . .	88·385
	<hr/>
	100·081

E. Soil from a district in Holland, where flax is well-grown :—

	Composition per cent.
Potash . . . . .	0·583
Soda . . . . .	0·306
Peroxide of iron . . . . .	6·047
Oxide of manganese . . . . .	a trace
Alumina . . . . .	5·626
Lime . . . . .	3·043
Magnesia . . . . .	0·105
Sulphuric acid . . . . .	0·023
Phosphoric acid . . . . .	0·159
Chloride of sodium . . . . .	0·023
Organic matter and water } not expelled at 212° . . . . .	5·841
Clay . . . . .	17·080
Sand . . . . .	60·947
	<hr/>
	99·783
Loss . . . . .	0·217
	<hr/>
	100·000

Mr. Marshall was also kind enough to forward to me a specimen of the kind of soil which is found deposited in the Humber, and the gradual silting up of which has formed the extensive flat districts reclaimed along that eastern coast. This specimen of soil, or *warp*, as it is termed, from the operation by which the ground becomes permanently gained from the sea, had not yet borne any crop. It is from Crowle, in Lincolnshire.

Its composition per cent. was found to be as follows :—

Potash . . . . .	0·534
Soda . . . . .	0·083
Peroxide of iron . . . . .	4·500
Oxide of manganese . . . . .	a considerable trace
Alumina . . . . .	3·065
Lime . . . . .	5·538
Magnesia . . . . .	0·052
Sulphuric acid . . . . .	0·113
Phosphoric acid . . . . .	0·222
Chloride of sodium . . . . .	0·067
Organic matter and water } not expelled at 212° . . . . .	5·328
Sand . . . . .	80·702
	<hr/>
	100·204

By these analytical results, it is abundantly evident how completely due to artificial means is the fertility of those different Belgian soils; the large quantity of azotized organic matter, the proportionally large quantities of phosphoric acid and magnesia, and of the alkalies, being evidently the result of the copious treatment with animal manures, to which, as all persons conversant with Flemish agriculture are aware, the soil in Belgium is subjected. This will become still more evident, when hereafter I have to notice the course of cultivation which those soils are made to undergo. The duty, so important in the preparation of our Irish soils for flax, of dividing the soil to the finest possible state, and rendering it perfectly friable and porous, is seen by the above results to be naturally effected in the Belgian soils, of which a well-manured, incoherent sand, might be more correctly the title; none of them containing, except that marked A, and that from Holland, E, as much clay as would even justify the title of a light loam. There is, therefore, no doubt but that the soils most adapted for the successful growth of flax are of this very light and porous character; and that, in the selection of districts in this country into which the flax culture may be extended, this quality of lightness and permeability of soil is of the first importance.

The quantity of lime contained in the Belgian soils will be observed to be extremely small; but in that from Holland and from the Lincolnshire warped land it is much larger, indeed so as to constitute the most dominant earthy material. This has evidently had its cause in the source from whence these soils were derived, the silt deposited in shallow, quiescent waters by the sea, and which contains, mixed with sand, a proportion of comminuted shells or chalk. There is no positive evidence that this amount of lime is connected with any decided inferiority in the flax; but it is still worthy of attention, that the soil of the districts which have been longest and best known for the production of good flax have but a mere trace of lime in their constitution.

The comparatively large quantity of magnesia which the Belgian soils contain, and which is so remarkably contrasted with its inferior proportion in the warp soil, is, in my opinion, produced by the artificial manuring by animal liquids; and to this source also I attribute the great richness of these soils in phosphoric acid.

[To be continued.]

VII. *On the Colouring Matters of Madder.*  
*By Dr. SCHUNCK\*.*

THE organic colouring matters present such a wide field for inquiry, that it would require the labour of years to enable one person fully to elucidate their properties, or even to bring this department of organic chemistry into a state of development proportionate to the present condition of the science. The substances included under the name of colouring matters by no means agree in their chemical characteristics ; they merely coincide in being possessed of certain vivid colours, or in giving rise to coloured compounds. Strictly considered, some of them ought to be classed among the resins and others among the extractive matters ; and on the other hand, if we attempt a definition of the class according to their chemical characteristics, we shall find it impossible to exclude a large number of bodies, which, like tannin and catechin, are capable of giving rise under peculiar circumstances to brown substances, which in nowise differ in their general properties from the bright red colouring matters of archil, logwood, &c. Some colouring matters are presented to us ready formed in the different parts of plants and animals ; others are produced artificially from colourless substances, which undergo very complex changes during the process ; others arise spontaneously during the first stages of oxidation or putrefaction following the extinction of organic life. In the investigation of substances thus widely differing in properties and formation, it would be vain to expect at present anything approaching to general results in regard to the class as a whole. I must therefore content myself on this occasion with giving a short account of the results of some experiments which I have made on one branch of the subject, at the same time apologising for their present vague and undefined nature.

I have directed my attention in the first instance to madder, partly because the colouring matters contained in it are almost unknown, or rather worse than unknown, viz. known in such a manner as merely to mislead those who wish to inform themselves by the accounts given of them, and partly because madder is an article of such an immense importance in the art of dyeing that every discovery in relation to it acquires immediately a practical bearing.

It will be unnecessary for me to allude to the former numerous investigations of madder, except so far as to mention that Robiquet discovered in it a crystallized volatile colouring matter, which he called *Alizarin*, and that Runge described five colouring matters which he obtained from it, viz. *madder purple*, *madder red*, *madder orange*, *madder yellow* and *madder brown*. I may here state as one result of my investigation, that I agree with Runge in thinking that there is more than one colouring matter in madder, though I am of opinion that the substances which he enumerates and describes are not pure. Before however entering on this part of the subject, I shall first give the results at which I have arrived in regard to ali-

\* From Report of British Association for 1846.

zarin. Alizarin is doubtless the most interesting and the most definite in its nature of all the substances contained in madder. It also presents itself the most easily to the observer even on the most superficial examination. If we heat madder spread out in a thin layer on a metal plate without carrying the heat far enough to char the woody parts of the root, we shall in the course of a few hours find its surface covered with small red or orange-coloured crystals, which consist of alizarin. In the same way any extract of madder, whether with water, alcohol or alkalies, evaporated to dryness and gently heated, gives a crystalline sublimate of alizarin, which is variously coloured from a light yellow to a dark red or brown. Now one of the first points to be ascertained in regard to this body was whether it exists as such in the root, or whether it is formed by the process of sublimation. Robiquet, the discoverer, states that it pre-exists in the plant. He considered alizarin as the colouring principle of madder, and merely subjected it to sublimation for the purpose of purifying it. But his investigation presents us with no convincing proof of this opinion, for the extract of madder with water, alcohol, &c., from which he prepares his alizarin by sublimation, shows no trace of anything crystalline; and many chemists have asserted in consequence that it is a product of decomposition, being formed by the action of heat in the same way as pyrogallic, pyrotartaric acid, and many other bodies. I have however no hesitation in affirming that it exists in the plant as such, having in more than one way obtained it in a crystallized state without the intervention of heat. If we make an extract of madder with cold water, we obtain a brown fluid which produces no reaction on test-paper. After being exposed however to the action of the atmosphere for some hours, it acquires a distinctly acid reaction; and if it be now examined carefully, there will be found floating about in it a number of long hair-like shining crystals: these crystals are alizarin. If the fluid be still further exposed to the influence of the atmosphere, a yellow amorphous substance begins to separate, which I shall mention afterwards. This is succeeded by a gelatinous substance, and after some days a complete state of putrefaction ensues. It seems as if the alizarin in madder, or at all events that part which dissolves in the water, exists in combination with lime. On exposure to the atmosphere, there is formed, from some constituent of the root dissolved in the fluid through the instrumentality of the oxygen, some acid, which seizes hold of the lime in the solution and separates the bodies which are combined with the lime. Now the alizarin, being a body of very slightly acid properties, is separated first, and the other substances follow in succession. The fresher the madder is, the purer will be the alizarin, which separates on exposure to the atmosphere; in some instances it forms on the surface of the fluid a thick light yellow scum; but in most cases it is mixed with brown or red substances, from which it is separated with difficulty. It is therefore most advisable to separate the crystals which are deposited after twelve hours' standing, by filtration. These crystals are then washed from the filter and boiled with very dilute nitric acid until they have be-

come of a bright yellow colour. They are then dissolved in boiling alcohol, from which they separate on cooling in yellow transparent plates and needles having a strong lustre. Alizarin prepared in this way has the following properties:—It has a pure yellow colour without any admixture of red. It may be volatilized without leaving any residue. The vapour crystallizes on cooling in beautiful yellow plates and needles. It suffers hardly any change if exposed to the action of the most powerful reagents. It dissolves without change in cold concentrated sulphuric acid. Concentrated nitric acid hardly affects it even on boiling. It is not changed by chlorine. It is insoluble in water, but soluble in alcohol with a yellow colour. It dissolves in alkalies with a beautiful purple colour. Its compounds with the alkaline earths are red and slightly soluble in water. Its compounds with the earths and metallic oxides are insoluble in water and exhibit different shades of red. It imparts no colour to cloth mordanted with acetate of alumina or oxide of iron, on account of its insolubility in water. Very little alizarin is obtained in this way; perhaps one 1 gr. from 1 lb. of madder, though there is more of it contained in the root.

I shall now shortly describe two other colouring matters which I have obtained from madder. If an extract of madder be made with hot or cold water, and a strong acid, such as muriatic or sulphuric acid, be added to the fluid, a dark reddish-brown flocculent precipitate is produced. This precipitate was separated by filtration and washed until the acid was removed. On being treated with boiling water, a part of it dissolves with a brown colour. On adding a few drops of acid to the filtered solution a dark brown precipitate is produced, which seems to me to be a peculiar colouring matter similar in its properties to orcein, hematin and other soluble colouring matters. It dissolves in alkalies with a red colour, and is capable of imparting very lively colours to mordanted cloth. As far as I am aware it has not been described in the former investigations of this subject, though it seems to be the principal substance concerned in the production of the colours for which madder is used in the arts. I have however only examined it very slightly as yet. The residue left behind by the boiling water was treated with dilute boiling nitric acid, by which every trace of the preceding substance is destroyed, and the residue itself acquires a bright yellow colour and a more powdery consistence. This yellow powder contains alizarin, as is shown by its giving crystals of that substance on being gently heated; in fact it contains all the alizarin of the root, but mixed with another substance of an amorphous nature but very similar properties, from which it is difficult to separate it. By crystallising from alcohol no separation can be effected, as they are both about equally soluble in that menstruum. They also behave in a similar manner towards the alkalies, the earths and most of the metallic oxides. I have hitherto only succeeded in discovering one method of separating them, which is as follows:—The mixture of the two is dissolved in a little caustic potash. To the solution is added perchloride of iron, which produces a dark reddish-brown precipi-

tate consisting of peroxide of iron in combination with the two substances. Now on boiling this precipitate with an excess of perchloride of iron, the alizarate of iron dissolves, forming a dark brown solution, while the iron compound of the other substance remains behind. On adding muriatic acid to the filtered solution, the alizarin separates in yellow flocks and may be purified by crystallization from alcohol. The other substance, to which I have not yet given a name, is obtained by decomposing its iron compound, which remains behind on treating with perchloride of iron, with muriatic acid, and washing till all the oxide of iron is removed. It seems also to be a colouring matter, as it dissolves with a red colour in alkalies and gives red compounds with the earths and metallic oxides. It is insoluble in water, but soluble in alcohol with a yellow colour. It therefore resembles the resins in its general properties. It cannot be obtained in a crystallized state. From a hot concentrated solution in alcohol it separates on cooling as a yellow powder. It imparts no colour to mordanted cloth.

### VIII. Comparative Analysis of the Urine of the Calf and the Sheep\*.

**M.** BRACONNOT finds that the urine of the calf, nourished by the milk of the mother, consists of—

	grs.
Ammoniaco-magnesian phosphate . . . . .	0·18
Chloride of potassium . . . . .	3·22
Sulphate of potash . . . . .	0·44
Urinary animal matter }	
Urea . . . . . }	2·36
Phosphate of iron . . . . .	
Phosphate of lime . . . . .	
Phosphate of potash . . . . .	
Combustible acid combined with potash . . .	traces
Silica . . . . .	
Mucus . . . . .	
Chloride of sodium ? . . . . .	
Water . . . . .	993·80
	<u>1000·00</u>

A litre of the urine of the sheep yielded—

Chloride of potassium . . . . .	6·13
Sulphate of potash . . . . .	3·74
Carbonate of magnesia . . . . .	1·40
Urea . . . . .	
Urinary animal matter . . . . .	
Hippurate of potash . . . . .	
Bicarbonate of potash . . . . .	
Carbonate of lime . . . . .	
Mucus . . . . .	
Oxide of iron . . . . .	
	quantities undetermined.

\* From the *Annales de Chimie et de Physique*, Juin 1847.  
*Phil. Mag.*, S. 3. Vol. 31. No. 205. July 1847. E

**IX. On the expected Reappearance of the celebrated Comet of 1264 and 1556. By Mr. HIND\*.**

THE time is now near at hand when the return of the comet of 1264 and 1556, signalised by Mr. Dunthorne and M. Pingré, may be expected to take place. It is therefore desirable that observers should be in possession of everything that may tend to facilitate their search for the comet; and I venture to communicate to the Society the results of some recent calculations of my own on the subject, preceded by a very brief view of the principal circumstances connected with former appearances of the comet, and a short notice of calculations already published.

“The great and celebrated comet” of 1264, as Pingré terms it, is mentioned by nearly all the European historians of the time, and was observed by the astronomers of the dynasties then reigning in the north and south of China. It is described as presenting a most imposing appearance, with a tail 100° in length, stretching from the east part of the “mid-heaven.” The comet was of “surprising magnitude,” far exceeding any remembered by those who beheld it. Contemporary writers generally considered it the precursor of the death of Pope Urban IV., and many of them relate that it disappeared on the same night that the pope died, or on October 2; thus, in the words of Thierri de Vaucouleurs,

“Quo (Urbano) moriente, velut mortem cognosceret ejus,  
Apparens minimè stella comata fuit.”

In 1556 the appearance of the comet was not on the same scale of splendour as in 1264, but still was sufficiently imposing to call forth from historians the epithets “*ingens et lucidum sidus*.” It was observed by Paul Fabricius, a mathematician and physician at the court of the emperor Charles V. of Austria. M. Pingré, the celebrated cometographer, sought in vain for the original observations; the only information he could find on the subject was contained in a small rough chart found in Lycosthenes and other authors. I have before† suggested the probability that these observations were given by Fabricius in his work upon the comet, published at Nürnberg in 1556, and mentioned by Lalande in his *Bibliographie*; but, as far as I am aware, this work has not been discovered in any library. M. Pingré would have at his command the splendid collections of St. Geneviève and the Royal Library at Paris; and his ineffectual search for the observations in these libraries makes it at least doubtful whether they are now in existence. The chart just mentioned enables us to form a tolerably definite

\* From the Proceedings of the Royal Astronomical Society, No. 14.

† *Ast. Nach.* 493.

idea of the path followed by the comet, and we have ample information for a rough determination of the elements.

When Halley published his Synopsis of Cometary Astronomy, he gave a set of parabolic elements for the comet of 1556, founded upon the observations made by Paul Fabricius; but he remarks that these elements are not so certain as those of other comets he had computed, the observations being made "neither with sufficient instruments nor due care," and by no means to be reconciled with any regular calculation.

The elements of the comet of 1264 were first computed by Mr. Dunthorne. His discussion of the observations and circumstances relating to the comet's apparition are published in vol. xlvii. of the Philosophical Transactions. The elements are chiefly founded on the authority of a manuscript preserved in the library of Pembroke Hall College, Cambridge, entitled *Tractatus fratris Egidii de Cometis*. But it must be observed there are manifest contradictions in this account not easily set right. The other authorities consulted were the *Chronicon Sampetrinum Erphurtense* and the Chronicle of John Vitoduranus. The orbit deduced by Mr. Dunthorne much resembles that calculated by Halley for the comet of 1556.

In the Memoirs of the Royal Academy of Sciences at Paris for 1760, appears a valuable memoir by M. Pingré on the comet of 1264. After collecting together a great number of accounts from different chronicles and histories of the day, he proceeds to the discussion of the elements. The contradiction in the Cambridge manuscript which relates to the comet's motion in longitude is pointed out; and since this manuscript was Mr. Dunthorne's chief authority, it might be supposed that his orbit would differ entirely from M. Pingré's. This, however, was not the case; for although there are differences of some moment in one or two of the elements, there is still a striking similarity between the two orbits taken as a whole, and M. Pingré's approaches much nearer than Mr. Dunthorne's to the orbit of the comet of 1556. A closer agreement might have been produced if he had not wished to preserve the path laid down by Thierri de Vaucouleurs with as little alteration as possible. M. Pingré concludes from his researches that there is little doubt of the identity of the comets of 1264 and 1556, and, therefore, that the return to perihelion may be expected to take place in the year 1848. In No. 493 of the *Astronomische Nachrichten* will be found the results of my first calculations relating to this comet. I have there deduced elements from the observations by Fabricius in 1556, and computed an ephemeris for comparison with the comet's observed path. The agreement, though not so close as could be wished, was the best that could be obtained from the data

given by M. Pingré in his *Cometography*. I then reduced the elements to the year 1264, and with the assistance of a passage in Thierri's poem, I fixed the time of perihelion for July 9·9 (old style). The passage alluded to is as follows :—

“ Undecimumque gradum Phœbo superante Leonis,  
Ter deno Cancri restitit illa loco.”

With M. Pingré, I have understood by “ *Ter deno Cancri*,” the 120th degree of longitude; but I am not quite sure that this is the true interpretation.

With perihelion and node reduced as before stated, and the other elements as for 1556, an ephemeris of the comet's geocentric path in 1264 was computed. During the month of July, calculation and observation agree pretty well; but after the beginning of August the theoretical places entirely differ from the positions of the comet, as deduced from the accounts. Instead of traversing Orion towards the end of its appearance, as some historians relate, it would take a higher declination, passing through Auriga and Taurus.

Since the publication of this paper in the *Astronomische Nachrichten*, I have made some further investigations on the subject, and with more success than in my first calculations. A closer comparison of data showed pretty clearly that the observation of March 5, on which I had chiefly relied, must be erroneous as it is given by M. Pingré. In tome i. of his *Cometography*, p. 503, we learn that on March 5 the comet was almost in the right line joining the stars  $\gamma$  and  $\theta$  Virginis, and was equidistant from the stars. A trigonometrical calculation from these data gives the place of the comet in longitude  $188^{\circ} 1'$ , and latitude  $+2^{\circ} 19'$ , and this position was employed in my earlier investigations. But I have recently satisfied myself, that the observation as given above cannot be reconciled with those of March 3 and 4, and on subsequent days, by any set of elements. The cause of this anomaly is, I believe, an error in the name of the star. If instead of  $\gamma$  and  $\theta$  Virginis we read  $\delta$  and  $\theta$ , then the place of the comet would be in longitude  $188^{\circ} 41'$ , and latitude  $+5^{\circ} 13'$ , which agrees very well with the track which the comet ought to have followed, according to the other observations.

A recalculation of the elements from an interpolated position for March 5, and from those of March 9 and 14, gives the following values :—

Passage through perihelion, 1556, April 22·0233, G. M. T. [Old style.]

Longitude of perihelion .....	$274^{\circ} 14\cdot9$	Equinox of 1556.
Ascending node .....	$175^{\circ} 25\cdot8$	
Inclination .....	$30^{\circ} 12\cdot2$	
Log. least distance.....	9·70323	
	Motion direct.	

The following ephemeris of the comet for the appearance in 1556, Greenwich mean midnight, old style, is deduced from these elements:—

1836. Old style.	Geo. long.	Geoc. lat.	Log. $r.$	$\Delta.$
March 3	188° 13'	+ 1° 9'	0.0732	0.193
4	188 0	3 40	0.0670	0.175
5	187 44	6 45	0.0606	0.157
6	187 22	10 36	0.0541	0.140
7	186 54	15 29	0.0476	0.124
8	186 14	21 43	0.0409	0.109
9	185 18	29 49	0.0341	0.096
10	183 49	40 12	0.0272	0.085
11	181 11	52 50	0.0201	0.078
12	175 21	67 5	0.0130	0.075
13	153 35	80 29	0.0057	0.078
14	55 19	82 30	9.9983	0.085
15	27 16	73 26	9.9908	0.095
16	20 37	65 30	9.9831	0.108
17	17 44	59 16	9.9753	0.122
27	12 19	34 58	9.8903	0.302
April 6	12 7	27 1	9.7959	0.505
16	14 13	20 30	9.7178	0.733
26	19 12	+13 52	9.7130	0.974

If this ephemeris be compared with the descriptions of the comet's apparent path in the heavens, we shall find the agreement as close as could be expected, considering the uncertainty and irregularity of the data.

With the above elements reduced to 1264, the time of perihelion was found to be July 13°42, *i. e.* assuming with Pingré, that the comet was in longitude 120° when the sun had reached the 11th degree of Leo, according to the narration of Thierri de Vaucouleurs. The geocentric places of the comet, Greenwich mean midnight, old style, would then be as follows:—

1264. Old style.	Geo. long.	Geoc. lat.	$r.$	$\Delta.$
July 7	138° 10'	+18° 14'	0.53	0.82
17	132 36	22 9	0.51	0.62
22	126 29	21 54	0.55	0.55
27	118 36	20 14	0.61	0.48
Aug. 6	101 14	+10 17	0.75	0.41
16	85 23	-3 47	0.92	0.39
26	70 47	17 10	1.09	0.42
Sept. 5	56 39	27 8	1.26	0.48
15	43 11	33 4	1.43	0.57
25	31 35	35 26	1.59	0.69
Oct. 5	22 47	-35 30	1.75	0.84

If we are to depend solely on the European accounts of this comet's path, the above is liable to two objections: first, too high a declination in August; and secondly, that the posi-

tions are in Eridanus during the latter part of the comet's apparition; historians generally contenting themselves with stating that the comet "finally traversed Orion." M. Pingré's elements, which are not open to these objections, do not agree so well as mine with the more circumstantial details left us in the Chinese annals. The two orbits differ chiefly in the longitude of the node and perihelion distance, but the discordances are by no means great.

The results of my calculations have satisfied me that the comet of 1264 was, in all probability, the same as that of 1556, and consequently, that its return to perihelion must be very near at hand. The nodes of the comet's orbit lie very close to the earth's path. The ascending node is passed fifty days before perihelion, the radius vector being 1.193, and consequently the distance outside the earth's orbit about 0.197. The passage through descending node occurs  $31\frac{1}{2}$  days after perihelion, and the distance of the point from the earth's orbit inside is 0.126. However, the nearest approach of the comet to the earth will not happen at the nodes, but soon after its passage through them; thus in 1556 the least distance between the two bodies was 0.074, nine days after the transit through ascending node. The effect of this close proximity to our globe on the period of revolution of the comet has been investigated by Professor Mädler, of the Dorpat Observatory, as detailed in No. 501 of the *Astronomische Nachrichten*; it amounted to  $14\frac{1}{2}$  days only, and the return of the comet to perihelion was fixed for the end of February 1848.

The following table contains the heliocentric co-ordinates referred to the equator and the log. radii vectores of the comet in my last orbit, reduced to 1848, for every tenth day, from ninety days before to 90 days after perihelion.

Time from perihelion pass. Days.	<i>x.</i>	<i>y.</i>	<i>z.</i>	Log. <i>r.</i>
-90	-1.7430	+0.5750	-0.0603	0.2640
80	1.6231	0.4370	0.0445	0.2257
70	1.4931	0.2963	0.0284	0.1826
60	1.3504	0.1533	-0.0122	0.1333
50	1.1917	+0.0084	+0.0041	0.0762
40	1.0120	-0.1363	0.0206	0.0092
30	0.8039	0.2770	0.0363	9.9300
20	0.5570	0.4031	0.0501	9.8385
-10	-0.2611	0.4907	0.0592	9.7474
0	+0.0738	0.4961	0.0583	9.7032
+10	0.3929	0.3951	0.0450	9.7474
20	0.6507	0.2266	0.0239	9.8385
30	0.8503	-0.0352	+0.0004	9.9300
40	1.0086	+0.1590	-0.0233	0.0092
50	1.1385	0.3490	0.0463	0.0762
60	1.2484	0.5331	0.0685	0.1333
70	1.3433	0.7109	0.0900	0.1826
80	1.4268	0.8828	0.1107	0.2257
+90	+1.5015	+1.0492	-0.1307	0.2640

With the above values for  $x$ ,  $y$  and  $z$ , and those of X, Y, Z, taken from the Nautical Almanac, the position of the comet for different suppositions as to the time of passage through perihelion may be readily obtained. If we suppose March 0, which is about the epoch fixed by Professor Mädler, we shall have the following ephemeris for facilitating the discovery of the comet, mean noon at Greenwich :—

1847—8.	R.A.	Decl.	$\Delta$ .
Dec. 1	187° 16'	-11° 22'	2.16
11	193 55	12 56	1.92
21	201 52	14 29	1.68
31	211 43	15 52	1.46
Jan. 10	224 16	16 50	1.26
20	240 18	16 47	1.11
30	259 53	15 3	1.02
Feb. 9	281 23	11 24	1.03
19	302 15	7 1	1.13
29	321 18	3 23	1.29
Mar. 10	338 5	- 0 54	1.48
20	352 11	+ 0 50	1.66
30	3 50	2 9	1.84
April 9	13 32	3 11	2.01
19	21 46	3 59	2.17
29	28 52	4 35	2.32
May 9	35 5	4 58	2.46
19	40 36	5 11	2.59
29	45 31	+ 5 12	2.69

It appears from this ephemeris, that according to the most probable supposition we can make respecting the time of perihelion without actual calculation of the perturbations, the position of the comet in the heavens during the approaching reappearance will be extremely unfavourable for observation ; and it is therefore the more desirable that those who look out for comets should be on the alert. Nearly the whole of the vast trajectory of this comet lies below the plane of the ecliptic, and *far from the paths of the larger planets*, but it extends into space more than twice the distance of Neptune ; and surely we are not yet able to say what causes may operate, at this immense distance from the sun, to affect the time of the next return to perihelion. If however the comet can be detected and observed, we shall then have the means of ascertaining something more on these points

X. *Analysis of the Water of the Thermal Spring of Bath (King's Bath).* By Messrs. GEORGE MERCK and ROBERT GALLOWAY\*.

THE water of this celebrated spring, the efficacy of which was known in the time of the Romans, has been analysed repeatedly by various chemists at different periods. Richard Phillips†, Scudamore‡, Walker§, and more recently Noad||, have occupied themselves in the investigation of this water. In their several analyses, the whole amount of the fixed ingredients of the water agrees very closely; but in regard to the composition of these substances there are considerable discrepancies, as may be seen in a table which we have annexed at the end of this paper.

Besides great differences in the quantitative analysis, we find discrepancies even in regard to the presence and absence of certain constituents. Among the chemists that have been mentioned, Walker is the only one who has recognised the presence of potash. The same chemist corroborated Scudamore's statement as to the presence of magnesia, overlooked by their predecessors; but he states also that he detected alumina, which none of the others found. In all these analyses iodine has been omitted. Mr. Cuff¶ however has indicated the presence of this element in the spring.

These discrepancies made another investigation of the mineral water of Bath very desirable; the following analysis was performed at the suggestion of Dr. A. W. Hofmann.

To obtain the water genuine, and especially for the purpose of ascertaining the amount of free carbonic acid it contained, we collected the water ourselves, an operation in which we were kindly assisted by Messrs. Green and Simms, lessees of the establishment.

The water was taken from the principal well, which supplies the King's and Queen's baths, which are the most esteemed and valued in the city. Of the two other wells, one supplies the Hot Bath and the other the Cross Bath, which are in the neighbourhood of those first mentioned.

\* Communicated by the Chemical Society; having been read Nov. 16, 1846.

† An Analysis of the Bath Water, by Richard Phillips. London, 1806.

‡ A Chemical and Medical Report of the properties of the Mineral Waters of Buxton, Matlock, &c., by Ch. Scudamore, M.D. 1820.

§ Quarterly Journal of Science, Literature and Arts, vol. xxvii. 78. 1829.

|| Pharmaceutical Journal, vol. iii. 526.

¶ Memoir on the occurrence of Iodine and Bromine in certain Mineral Waters of South Britain, by Charles Daubeny; Transactions of the Royal Society of London, 1830, ii. p. 223.

The King's Bath is an oblong cistern, 65 feet long and 40 feet broad, in which the water stands at the height of 46 inches. It is supplied from the bottom by means of twelve large and about twenty smaller apertures. By far the largest amount of water rises however from an opening made in the centre of the bath, 18 inches in diameter. Although the water flows under the influence of a very small pressure, the quantity is such, that the two reservoirs, the King's and the Queen's bath, are entirely filled in about nine hours. The quantity of water entering each minute is 126 gallons, upon the authority of Dr. Daubeny\*.

### I. Qualitative Analysis.

The water as it issues from the well has a temperature of  $46^{\circ}$  C. ( $115^{\circ}$  Fahr.), the temperature of the air being  $20^{\circ}$  C. ( $68^{\circ}$  Fahr.); it is clear and without odour, and has no effect upon vegetable colours; it has a saline and slight iron taste; the iron is deposited as sesquioxide in rather large quantities in the pipes leading from the well.

The following experiments gave the qualitative composition of the mineral water; on boiling for some time a white crystalline precipitate formed. The qualitative analysis was therefore divided into two parts.

- a. The analysis of the precipitate formed on boiling.
- b. The analysis of the substances remaining dissolved.

#### *a. Analysis of the Precipitate formed on boiling.*

1. The precipitate was treated with hydrochloric acid; a small portion of it dissolved with effervescence, indicating the presence of carbonic acid. The portion insoluble in hydrochloric acid dissolved on the addition of a large quantity of water:—*Indicating sulphate of lime.*

Another portion of the water was boiled some time, with the precaution of replacing the evaporated water, in order that all the sulphate of lime should remain in solution; in this case only a very small precipitate was formed, which was entirely soluble in hydrochloric acid.

2. On heating this solution and adding ammonia, a very slight flocculent precipitate of a yellowish-white colour was produced after some time:—*Indicating oxide of iron.*

3. In the filtrate from the sesquioxide of iron (2.), on the addition of oxalate of ammonia, a white precipitate was formed:—*Indicating salts of lime.*

\* On the Quantity and Quality of the Gases disengaged from the Thermal Spring which supplies the King's Bath in the City of Bath, by Charles Daubeny; *Transactions of the Royal Society of London*, 1834, I. i.

4. In the liquid filtered off from the oxalate of lime (3.), phosphate of soda produced an exceedingly slight crystalline precipitate :—*Showing the presence of magnesia.*

*Note.*—This precipitate could only be distinctly seen in testing a large quantity of the water.

*b. Analysis of the substances remaining dissolved.*

The liquid which was filtered from the precipitate (a.) formed on boiling had no alkaline reaction ; a portion of it was evaporated nearly to dryness and treated with hydrochloric acid ; no carbonic acid was evolved, from which compartment the absence of alkaline carbonates could with safety be concluded.

1. A portion of the liquid gave on addition of chloride of barium a copious white precipitate, insoluble in hydrochloric acid :—*Indicating sulphuric acid.*

2. In another portion of the liquid nitrate of silver produced a copious white precipitate, easily soluble in ammonia :—*Evidencing the presence of chlorine.*

3. The entire solubility of the silver precipitate seemed to indicate the absence of iodides. To make ourselves perfectly certain of the absence of these salts, 30 or 40 pounds of the water were evaporated to 2 or 3 pounds, and the liquid filtered off from the precipitate which had been formed ; a part of this fluid was evaporated with precaution to dryness, the residue was mixed with some starch paste, and a few drops of nitric acid being added, feeble but distinct violet spots were observed : this experiment was repeated several times with the same success :—*Indicating the presence of iodine.*

4. Another portion of the liquid (b.) was treated with hydrochloric acid, evaporated to dryness, and gently ignited : on treating the residue with a large quantity of water an insoluble portion remained :—*Showing the presence of silicic acid.*

5. Another portion of the liquid (b.) gave, on addition of chloride of ammonium and oxalate of ammonia, a white precipitate :—*Indicating lime.*

6. On adding, to a portion of the filtrate, ammonia and phosphate of soda, a slight crystalline precipitate was formed :—*Indicating magnesia.*

7. For the discovery of the alkalies, the remaining portion of the filtrate from the lime precipitate was evaporated to dryness, and the residue ignited until the ammoniacal salts had been expelled. The ignited residue was then dissolved in water, the sulphuric acid and magnesia precipitated by baryta water, and after separation of the excess of baryta by means of carbonate of ammonia, the filtrate evaporated to dryness

and ignited. The residue imparted a yellow colour to the blowpipe flame :—*Evidencing the presence of soda.*

An alcoholic solution of the residue gave with a concentrated solution of bichloride of platinum a yellow crystalline precipitate :—*Indicating potassa.*

The precipitate which had formed on evaporating for the iodine determination, was treated with hydrochloric acid, the filtrate saturated with ammonia and precipitated by sulphide of ammonium ; this precipitate was re-dissolved in nitro-hydrochloric acid mixed with chloride of ammonium, and the sesquioxide of iron separated by ammonia. The filtrate, evaporated and fused with nitrate of potash and carbonate of soda, gave a green mass :—*Showing traces of manganese.*

Lithia, alumina, bromine and phosphoric acid were found to be absent.

In regard to the presence of gases in the water, it was scarcely necessary to test for the presence of free carbonic acid. On mixing a solution of lime with the mineral water a precipitate was formed, which dissolved in an excess of the mineral water. The quantity of free carbonic acid however is not very large ; the water has no reaction on blue vegetable colours ; hydrosulphuric acid is not contained in the water. Acetate of lead gave only a white precipitate of sulphate of lead free from all trace of brown colour, which might indicate the presence of sulphur.

A large quantity of gas is continually disengaged from the chief spring as well as from the secondary ones. Dr. Daubeny\* paid particular attention to the composition of this gas. He found that it consists principally of nitrogen, together with small quantities of carbonic acid and oxygen.

He employed a peculiar apparatus, constructed on purpose for these experiments, by which he was enabled to collect the whole of the gases from the principal well, as well as from those adjoining it. The experiments of Daubeny are so numerous and accurate as to preclude any other researches on the subject.

## II. Quantitative Analysis.

### *Determination of the Specific Gravity.*

A small bottle, which contained at the temperature of  $16^{\circ}5$  C. ( $60^{\circ}$  Fahr.) 10 grms. of distilled water, contained at the same temperature 10.025 grms. of the mineral water ; from this the specific gravity of the water is calculated as 1.0025.

\* Vide Memoir mentioned.

*1. Estimation of Sulphuric Acid.*

The mineral water was heated with a little hydrochloric acid and chloride of barium added.

I. 534·199 grms. of water gave 1·340 grm. of sulphate of baryta = 0·4605 grm., or 0·08620 per cent. of sulphuric acid.

II. 475·003 grms. of water gave 1·1791 grm. of sulphate of baryta = 0·4050 grm., or 0·08526 per cent. of sulphuric acid.

Mean of the results, 0·08573 per cent.

*2. Estimation of Chlorine.*

The water was treated with nitric acid and precipitated by nitrate of silver; the precipitated chloride of silver was washed by decantation, fused and weighed.

I. 101 grms. of water gave 0·1137 grm. of chloride of silver = 0·2811 grm., or 0·02778 per cent. of chlorine.

II. 100·006 grms. of water gave 0·1093 grms. of chloride of silver = 0·02702 grms., or 0·02701 per cent. of chlorine.

Mean of the results, 0·02739 per cent.

*3. Estimation of Silicic Acid.*

To the water was added nitric acid in excess; it was then evaporated to dryness and the residue for some time heated on the sand-bath. On treating this residue with water and hydrochloric acid, the silicic acid remained behind; it was collected, washed and weighed.

I. 765·325 grms. of the water gave 0·0342 grm., or 0·00446 per cent. of silicic acid.

II. 732·015 grms. of water gave 0·0289 grm., or 0·00407 per cent. of silicic acid.

Mean of the results, 0·00426 per cent.

*4. Estimation of Iron.*

The iron was estimated,—

- In the precipitate formed on boiling the mineral water.
- In the water which had not been boiled.

Both estimations gave the same results.

A. Estimation of the iron in the precipitate :—

A certain quantity of the water was boiled for some time; the precipitate which had formed was washed, dissolved in hydrochloric acid and precipitated by an excess of ammonia.

I. 777·215 grms. of water gave 0·0079 grm., or 0·00101 per cent. of sesquioxide of iron.

B. Estimation of the iron in the water which had not been boiled :—

The liquid filtered off from the silicic acid (3.) was concentrated and precipitated by an excess of ammonia.

II. 765·325 grms. of water gave 0·0078 grm., or 0·00101 per cent. of sesquioxide of iron.

III. 732·015 grms. of water gave 0·0086 grm., or 0·00116 per cent. of sesquioxide of iron.

Mean of the results, 0·00106 per cent., corresponding to 0·00153 per cent. of carbonate of oxide of iron.

### 5. *Estimation of Lime.*

The estimation of the lime was divided into—

A. Estimation of the lime contained in the water in the state of carbonate.

B. Estimation of the lime contained in the water in the state of sulphate.

C. Estimation of the total amount of lime for control.

A. Estimation of the lime combined with carbonic acid :—

The ammoniacal liquor filtered off from the precipitate of sesquioxide of iron was precipitated by oxalate of ammonia; the oxalate of lime was converted in the known way into carbonate.

I. 712·747 grms. of water gave, on boiling, a precipitate containing 0·0904 grm. of carbonate of lime = 0·05062 grm., or 0·00712 per cent. of lime.

II. 623·881 grms. of water gave, on boiling, a precipitate containing 0·0782 grm. of carbonate of lime = 0·0437 grm., or 0·00700 per cent. of lime.

Mean of the results, 0·00706 per cent.

B. Estimation of the lime combined with sulphuric acid :

The mineral water was kept boiling for one or two hours, replacing the water which evaporated; the precipitate formed was filtered off, washed, and to the filtrate was added chloride of ammonium, ammonia, and oxalate of ammonia; the oxalate of lime was converted into carbonate.

I. 710·747 grms. of water gave in this way 0·6072 grm. of carbonate of lime = 0·3400 grm., or 0·04783 per cent. of lime.

II. 623·881 grms. of water gave 0·5165 grm. of carbonate of lime = 0·2892 grm., or 0·04635 per cent. of lime.

Mean of the results, 0·04709 per cent.

C. Estimation of the total amount of lime for control :—

The ammoniacal liquid which was filtered off from the precipitate of sesquioxide of iron was precipitated after the addition of chloride of ammonium by oxalate of ammonia, and the oxalate of lime converted into carbonate.

I. 765·325 grms. of water gave 0·7211 grm. of carbonate of lime = 0·403816 grm., or 0·05276 per cent. of lime.

II. 732·015 grms. of water gave 0·6981 grm. of carbonate of lime = 0·3909 grm., or 0·05340 per cent. of lime.

Mean of the results, 0·05308 per cent.

Mean of the lime combined with carbonic acid 0·00706

Mean of the lime combined with sulphuric acid 0·04709

Total amount found by addition 0·05415

Mean of the total amount found by direct estimation . . . . . } 0·05308

### 6. Estimation of Magnesia.

The estimation of the magnesia was divided in the same manner as the estimation of lime into—

A. Estimation of the magnesia combined with carbonic acid.

B. Estimation of the magnesium combined with chlorine.

C. Estimation of the total amount of magnesia for control.

A. Estimation of magnesia contained in the water as carbonate:—

To the liquid filtered off from the oxalate of lime was added phosphate of soda; on stirring, after some time a precipitate of phosphate of magnesia and ammonia was formed, which was converted by ignition into pyrophosphate of magnesia.

I. 777·215 grms. of water gave, on boiling, a precipitate which contained 0·0046 grm. of pyrophosphate of magnesia = 0·001685 grm., or 0·00021 per cent. of magnesia.

II. 623·881 grms. of water gave, on boiling, a precipitate which contained 0·0044 grm. of pyrophosphate of magnesia = 0·00016 grm., or 0·00025 per cent. of magnesia.

Mean of the results, 0·00023 per cent.

B. Estimation of the magnesia contained in the water as chloride of magnesium.

The liquid filtered off from the oxalate of lime was concentrated by evaporation, ammonia added filtered off from a small portion of silicic acid which separated, and the magnesia precipitated by phosphate of soda.

I. 414·279 grms. of water gave in this way 0·1007 grm. of pyrophosphate of magnesia = 0·03689 grm., or 0·008906 per cent. of magnesia.

II. 427·1 grms. of water gave 0·1050 grm. of pyrophosphate of magnesia = 0·03846 grm., or 0·009004 per cent. of magnesia.

Mean of the results, 0·008955 per cent.

C. Estimation of the total amount of magnesia for control :—

The liquid filtered off from the precipitate of oxalate of lime was concentrated, ammonia and phosphate of soda added.

I. 765·325 grms. of water gave 0·1936 grm. of pyrophosphate of magnesia = 0·070929 grm., or 0·00926 per cent. of magnesia.

II. 732·015 grms. of water gave 0·1837 grm. of pyrophosphate of magnesia = 0·0673 grm., or 0·00919 per cent. of magnesia.

Mean of the results, 0·00922 per cent.

Mean of the magnesia combined with carbonic acid 0·00023

Mean of the magnesia contained in the water as }  
chloride of magnesium . . . . . } 0·00895

Total amount found by addition 0·00918

Mean of the total amount found by direct estimation 0·00922

### *7. Estimation of the Alkalies.*

For the estimation of the alkalies the mineral water was evaporated to one-third of its volume and baryta water added in excess, the precipitates of sulphates of baryta, lime, magnesia and sesquioxide of iron were filtered off, and the excess of baryta precipitated by means of carbonate of ammonia. To get rid of the silicic acid the filtrate was evaporated to dryness with hydrochloric acid, gently ignited, dissolved in water, again filtered and evaporated to dryness ; the mixed chlorides obtained in this manner were weighed.

I. 632·481 grms. of the mineral water gave 0·2937 grm. of chloride of sodium and chloride of potassium = 0·04643 per cent. of the mixed chlorides.

II. 546·032 grms. of water gave 0·2538 grm. of chlorides of sodium and potassium = 0·04648 per cent. of the mixed chlorides.

Mean of the results, 0·04645 per cent.

### *8. Estimation of the Potassa.*

The chlorides of potassium and sodium were dissolved in a small quantity of water and an excess of bichloride of platinum added ; the liquid was then evaporated to dryness in the water-bath, the residue digested with alcohol, the insoluble chloride of platinum and potassium filtered off from the soluble sodium salt and washed with alcohol ; the precipitate was dried in the water-bath and weighed.

I. 632·481 grms. of the mineral water, or 0·2987 grm. of the mixed chlorides, gave 0·124 grm. of chloride of platinum

and potassium = 0·0378 grm. of chloride of potassium = 0·00597 per cent. of chloride of potassium, which equals 0·00377 per cent. of potassa.

II. 546·032 grms. of water, or 0·2538 grm. of the mixed chlorides, gave 0·0975 grm. of chloride of platinum and potassium = 0·02977 grm. of chloride of potassium = 0·00545 per cent. of chloride of potassium, which equals 0·00342 per cent. of potassa.

Mean of the results, 0·00571 per cent. of chloride of potassium and 0·0359 per cent. of potassa.

### 9. Estimation of the Soda.

The quantity of soda was found simply by the difference of the mixed chlorides and the quantity of chloride of potassium found by direct estimation.

Mean of the mixed chlorides . . . .	0·04645
Mean of the chloride of potassium . .	<u>0·00571</u>
Chloride of sodium . . . .	0·04074

corresponding to 0·02168 per cent. of soda.

### 10. Estimation of Carbonic Acid.

To find the quantity of free carbonic acid contained in the water at the moment it was taken from the well, a siphon of exactly known capacity was immersed in the well, and the water obtained in this way put in bottles, containing a mixture of ammonia and chloride of calcium. In this way the free carbonic acid as well as the carbonic acid in combination was precipitated in the form of carbonates. Four bottles were filled with mineral water by this method. The capacity of the siphon was exactly 533 cubic centimetres, therefore  $533 \times 4 \times 1\cdot0025 = 2137$  grms. of water were taken.

The precipitate from the water contained in these four bottles was collected, washed, dried and weighed; it yielded 1·4748 grm. of carbonate mixed with some alumina from impurity in the solution of chloride of calcium.

To estimate the quantity of carbonic acid in this precipitate, two portions of it were taken and estimated separately after the method proposed by Drs. Fresenius and Will.

I. 0·66 grm. of the carbonate, &c. gave in this way 0·22 grm. of carbonic acid, therefore 1·4748 grm. of the carbonate, or 2137·0 grms. of water, gave 0·4916 grm. of carbonic acid.

II. 0·718 grm. of the carbonate, &c. gave 0·23 grm. of carbonic acid, therefore 1·4748 grm. of the carbonate, &c., or 2137·0 grms. of water, gave 0·4718 grm. of carbonic acid.

*Mean of the results.*

0·4817 grm. of carbonic acid, which equals	0·02254 per cent.
Total amount of carbonic acid . . .	0·02254
Carbonic acid existing in combination—	
With oxide of iron . . . .	0·00057
With lime . . . . .	0·00554
With magnesia . . . .	<u>0·00024</u>
Sum total . . . . .	<u>0·00635</u>
Free carbonic acid remaining	0·01619

From the details contained in the preceding pages, it follows that the thermal spring in the King's Bath contains the following constituents in 100 parts:—

Carbonate of lime . . . .	0·01260
Carbonate of magnesia . . .	0·00047
Carbonate of oxide of iron .	0·00153
Sulphate of lime . . . .	0·11436
Sulphate of potassa . . . .	0·00663
Sulphate of soda . . . .	0·02747
Chloride of sodium . . . .	0·01806
Chloride of magnesium . . .	0·02083
Silicic acid . . . . .	<u>0·00426</u>
	0·20620

Traces of manganese and iodine.

*Estimation of the total amount of the fixed ingredients in the water for control.*

The water was concentrated in a porcelain dish, and afterwards evaporated to dryness in a platinum basin. The residue was heated in an air-bath until the weight was constant. Two estimates were made.

I. 217·058 grms. of water gave 0·4540 grm., or 0·20916 per cent. of residue.

II. 319·57 grms. of water gave 0·6726 grm., or 0·21040 per cent. of residue.

Mean of the results, 0·20978 per cent.

But in this experiment the iron was obtained in the state of sesquioxide, whilst in the preceding calculation it is taken as the carbonate of the oxide, in which form it exists in the water.

On calculating the absolute weights from the above, we obtain the following numbers:—

	In a litre.	In an imperial gallon (70,000 grs.).
Carbonate of lime . . . .	0·1260 grm.	8·82000 grs.
Carbonate of magnesia . . . .	0·0047 ...	0·32900 ...
Carbonate of oxide of iron . . . .	0·0153 ...	1·07100 ...
Sulphate of lime . . . .	1·1436 ...	80·05200 ...
Sulphate of potassa . . . .	0·0663 ...	4·64100 ...
Sulphate of soda . . . .	0·2747 ...	19·22900 ...
Chloride of sodium . . . .	0·1806 ...	12·64200 ...
Chloride of magnesium . . . .	0·2083 ...	14·58100 ...
Silicic acid . . . . .	0·0426 ...	2·98200 ...
	<hr/>	<hr/>
	0·20621 ...	144·01800 ...

According to our experiments, 1 litre of the water contains 95·64 cubic centimetres of free carbonic acid at the temperature of 46° C. (115° F.) and normal atmospheric pressure.

One imperial gallon contains therefore 26·45 cubic inches of free carbonic acid of 46° C., being more than double the quantity which has been determined by former experiments.

This however is not surprising, as the estimations previously made had been effected by the expulsion of the carbonic acid from the water. Besides the difficulty of avoiding a loss of carbonic acid before the operation, it is scarcely possible, as Mr. Phillips justly notices in his paper, to expel all carbonic acid by simple ebullition. Besides, we see from the experiments of Daubeny, that the gas which escapes from the well contains at different periods highly varying amounts of carbonic acid. He found by several experiments that the King's Bath evolves on an average 267 cubic inches of gas per minute, or 223 cubic feet in twenty-four hours. He further ascertained that this gas consists nearly entirely of nitrogen, mixed with a small amount of oxygen and carbonic acid, and that these gases were generally in the following proportion:—

$$\begin{aligned} \text{Nitrogen} & . . . = 91\cdot 9 \\ \text{Oxygen} & . . . = 3\cdot 8 \\ \text{Carbonic acid} & = 4\cdot 3 \end{aligned}$$

In many instances, however, he observed as much as 7·4 to 8·2, and even once 11·5 parts of carbonic acid.

From these observations there is no doubt that the quantity of carbonic acid dissolved in the water is very variable.

In the following Table we give the analyses of former experimenters, calculated in an imperial gallon (70,000 grs.).

	Phillips.	Seudamore*.	Walker.	Noad.
Carbonate of lime .....	7.680	5.280	10.667	
Carbonate of oxide of iron	0.274	0.200	0.243	0.521
Carbonate of soda .....	.....	.....	.....	5.760
Sulphate of lime .....	86.400	98.320	81.624	96.240
Sulphate of potassa .....	.....	.....	2.927	
Sulphate of soda .....	14.400	1.520	19.371	
Chloride of sodium .....	31.680	12.240	15.122	27.456
Chloride of magnesium ..	.....	15.360	13.339	7.142
Alumina .....	.....	.....	0.150	
Silicic acid .....	1.960	1.920	3.233	3.360
Quantity directly observed	142.394 144.125	134.840 .....	146.676 147.622	140.479 149.72
Carbonic acid .....	11.52 cub. in.	.....	7.60 cub. in.	

Our analysis agrees, as may be seen, best with that of Walker. According to Professor Liebig's† arrangement of mineral waters, the thermal spring of Bath would belong to the saline waters containing carbonic acid.

## XI. Notices respecting New Books.

*On the Correlation of Physical Forces : being the substance of a Course of Lectures delivered in the London Institution, in the year 1843.*  
*By W. R. GROVE, Esq., M.A., F.R.S., Barrister-at-Law. Printed at the request of the Proprietors of the London Institution.* London : Samuel Highley, 32 Fleet Street.

THIS publication treats of subjects which might have been advantageously considered at much greater length ; but it must be acknowledged that in the brief space to which the author has confined the announcement of his views and speculations, he has done them no small degree of justice ; it may indeed be questioned whether the opinions broached are not of such a nature as to defy the test of experiment to realise or to refute them. This is certainly the case as far as experiment has yet been carried ; but although we discover great reason for doubting whether the difficulties which beset the subjects may ever be overcome, we discover no cause for despair, seeing that new modes of research and new instruments for carrying them out are of almost daily occurrence. As a proof of this we may cite the author's excellent invention of his well-known and justly-appreciated voltaic battery ; and his still more recent discovery, that water may be decomposed by heat so as to exhibit both its elements in the gaseous form.

Mr. Grove states that "the position which he seeks to establish in this Essay is, that the various imponderable agencies, or the affections of matter which constitute the main objects of experimental

\* Recalculated according to a more correct principle by Walker.

† *Handwörterbuch der Chemie*, Art. 'Analyse der Mineralwasser.'

physics, viz. heat, light, electricity, magnetism, chemical affinity and motion, are all correlative, or have a reciprocal dependence ; that neither, taken abstractedly, can be said to be the essential or proximate cause of the others, but that either may, as a force, produce or be convertible into the other ; thus heat may mediately or immediately produce electricity, electricity may produce heat ; and so of the rest."

In further illustration of the author's views, we may quote what he states to be the sense that he has attached to the word correlation, which is, that " of a reciprocal production or convertibility ; in other words, that any force capable of producing or being convertible into another, may, in its turn, be produced by it,—nay, more, can be itself resisted by the force it produces, in proportion to the energy of such production, as action is ever accompanied and resisted by reaction ; thus, the action of an electro-magnetic machine is reacted upon by the magneto-electricity developed by its action."

In order to support his speculations by facts, the author appeals in the first place to the agency of electricity. " To commence, then, with electricity as an initiating force, we get *motion* directly produced by it in various forms ; for instance in the attraction and repulsion of bodies, evidenced by mobile electrometers, such as that of Cuthbertson, where large masses are acted on ; the rotation of the fly wheel, another form of electrical repulsion, and the deflection of the galvanometer needle, are also modes of palpable, visible motion. Electricity directly produces *heat*, as shown in the ignited wire, the electric spark, and the voltaic arc, in the latter the most intense heat with which we are acquainted, so intense, indeed, that it cannot be measured, every sort of matter being dissipated by it. Electricity directly produces *light* in the same phenomena. It directly produces *magnetism* in all ferruginous bodies placed at right angles to its line of direction, and, indeed, in the substances, of whatever nature, traversed by the electrical current, in a direction at right angles to that of the current ; in this case giving us a new character of force, viz., a force acting, not in direct straight lines, but in a tangential or rather rectangular direction.

" Lastly, electricity directly produces *chemical affinity*, and by its agency we are enabled to obtain effects of analysis or synthesis, with which ordinary chemistry does not furnish us. Of these effects we have examples in the brilliant discoveries by Davy of the alkaline metals, and in the peculiar crystalline compounds made known by Crosse and Becquerel."

Having stated thus much respecting electricity in support of his peculiar views, Mr. Grove adduces additional confirmation of them from considering the action of light, in a passage which we shall quote at length. He observes that " light is, perhaps, that mode of force the reciprocal relations of which with the others has been the least traced out. Until the discoveries of Daguerre and Talbot, very little could be definitely predicated of the action of light in producing other modes of force ; and, even, since these discoveries, it is doubted by many competent investigators, whether the phenomena

of photography are not mainly dependent upon a separate agent accompanying light, rather than upon light itself. It is, indeed, difficult not to believe that a picture, taken in the focus of the camera obscura, and which represents to the eye all the gradations of light and shade shown by the original luminous image, is not an effect of light ; certain it is, however, that the different coloured rays exercise different actions upon various chemical compounds, and that the effects on many, perhaps on most of them, are not proportionate in intensity to the effects upon the visual organs ; those effects, however, appear to be more of degree than of specific difference, and without pronouncing myself positively upon the question, hitherto so little examined, I think it will be safer to regard the action on photographic compounds as resulting from a function of light : so viewing it, we get light as an initiating force, capable of producing, meditately or immediately, the other modes of force. Thus, it immediately produces chemical action ; and having this, we at once acquire a means of producing the others."

Mr. Grove then relates the following beautiful experiment, by which he conceives that he showed the production of all the other modes of force by light :—" A prepared Daguerreotype plate is inclosed in a box filled with water, having a glass front, with a shutter over it ; between this glass and the plate, is a gridiron of silver wire ; the plate is connected with one extremity of a galvanometer coil, and the gridiron of wire with one extremity of a Breguet's helix ; the other extremities of the galvanometer and helix are connected by a wire, and the needles brought to zero. As soon as a beam of either daylight or the oxyhydrogen-light is, by raising the shutter, permitted to impinge upon the plate, the needles are deflected : thus light being the initiating force, we get *chemical action* on the plate, *electricity* circulating through the wires, *magnetism* in the coil, *heat* in the helix, and *motion* in the needles."

We have had some difficulty in selecting passages for quotation from this publication, on account of the profusion of interesting matter which it contains, though in so small a space ; we believe, however, that the selections which we have given are such as will well and sufficiently illustrate the interesting views of their author.

## XII. *Proceedings of Learned Societies.*

### ROYAL SOCIETY.

[Continued from vol. xxx. p. 207.]

Feb. 11, "ON the Amount of the Radiation of Heat, at night, 1847. from the Earth, and from various Bodies placed on, or near the surface of the Earth." By James Glaisher, Esq. Communicated by G. B. Airy, Esq., F.R.S., Astronomer Royal, &c.

The author enters into a very detailed description of the construction of the thermometers he employed in these observations, and the precautions he took to ensure their accuracy ; and gives tabular records of an extensive series of observations, amounting to a num-

ber considerably above ten thousand, with thermometers placed on nearly a hundred different substances, exposed to the open air, under different circumstances, and in various states of the sky, at the Royal Observatory at Greenwich.

Feb. 18.—“On the Diurnal Variation of the Magnetic Declination of St. Helena.” By Lieut.-Colonel Edward Sabine, R.A., For. Sec. R.S.

It has long been known that the diurnal variation of the magnetic needle is in an opposite direction in the southern, to what it is in the northern hemisphere; and it was therefore proposed as a problem by Arago, Humboldt and others, to determine whether there exists any intermediate line of stations on the earth where those diurnal variations disappear. The results recorded in the present paper are founded on observations made at St. Helena during the five consecutive years, from 1841 to 1845 inclusive; and also on similar observations made at Singapore, in the years 1841 and 1842; and show that at these stations, which are intermediate between the northern and southern magnetic hemispheres, the diurnal variations still take place; but those peculiar to each hemisphere prevail at opposite seasons of the year, apparently in accordance with the position of the sun with relation to the earth's equator.

Feb. 25.—“On certain Properties of Prime Numbers.” By the Right Hon. Sir Frederick Pollock, M.A., F.R.S., Lord Chief Baron of the Exchequer, &c.

The author of this paper, after noticing Wilson's Theorem, (published by Waring about the year 1770, without any proof), which theorem is that, if  $A$  be a prime number,  $1. 2. 3. \dots (A-1) + 1$  is divisible by  $A$ ; refers to Lagrange's and Euler's demonstrations, and mentions Gauss's extension of the theorem, to any number, not prime; provided that instead of  $1, 2, 3, \&c.$   $(A-1)$ , those numbers only be taken which are prime to  $A$ , and 1 be either added or subtracted. This theorem was published by Gauss without a proof in 1801, with a rule as to the cases in which 1 is to be added or subtracted, the correctness of which is questioned by the author, who proceeds to propound the following theorem, which he had previously, for distinctness, divided into three.

If any number, prime or not, be taken, and the numbers prime to it, and less than one half of it be ascertained, and those be rejected whose squares  $\pm 1$  are equal to the prime number, or some multiple of it (which may be more than one), then the product of the remaining primes (if any),  $\pm 1$  shall be divisible by the prime number.

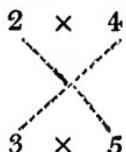
He gives as examples, 14, the primes to which, and less than one half, are 1, 3, 5, and  $1. 3. 5 = 15$ ; therefore  $1. 3. 5 - 1 = 14$ ; also 15, the primes to which and less, are 1, 2, 4, 7; but  $4 \times 4 = 16 = 15 + 1$ ; therefore 4 is to be rejected, and  $1. 2. 7 + 1 = 15$ . The author adds another theorem, that if  $A$  be a prime number, all the odd numbers less than it (rejecting as before); also, all the even numbers (making the same rejection except  $A-1$ ) will, multiplied together, be equal to  $A+1$ .

The author then proceeds to prove Gauss's extension of Wilson's

theorem, and to give the cases in which 1 is to be added or subtracted; and in the course of the proof, he mentions that the numbers prime to any number not only are found in pairs, one greater and one less than one-half of the number, but that they associate themselves in sets of four, with an odd pair in certain cases. Thus, the primes to 7 are 1, 2, 3, 4, 5, 6,—

$$2 \times 4 = 8 = 7 + 1.$$

Put the complementary numbers underneath crosswise, thus,—



so that  $2+5$  and  $4+3$  may equal 7; and then

$$3 \times 5 = 15 = 2 \times 7 + 1$$

$$2 \times 3 = 6 = 7 - 1$$

$$4 \times 5 = 20 = 3 \times 7 - 1$$

Multiplied together one way the product exceeds 7, or a multiple of it, by 1; multiplied the other way, the product is less than 7, or some multiple of it, by 1. By assuming the prime number to be A, and the two primes to it to be  $p, q$ , and that  $p+q$  be not equal to A, but  $pq=nA\pm 1$ , it is shown that the complementary primes  $(A-q)$  and  $(A-p)$  will have a product  $=n'A\pm 1$ , and that, instead of 1, the number may be any other prime to A. Upon this foundation the author proceeds to show that Wilson's theorem, and also Gauss's, may be made much more general; that if A be a prime number, as 7, the numbers less than it may be arranged in pairs, not only with reference to 1, but to any number less than 7. Take 4 as an example:—

$$\begin{array}{ccc} 1 & \times & 3 = 7 - 4 \\ & \diagup & \diagdown \\ 4 & \times & 6 = 4 \times 7 - 4 \\ & \diagdown & \diagup \\ 2 & \times & 5 = 2 \times 7 - 4 \end{array}$$

therefore  $1.2.3.4.5.6 = 7n - 4^3$ ;

therefore  $1.2.3.4.5.6 + 4^3 = 7n$ ; that is, is divisible by 7.

The same is then shown as to numbers not prime, provided those numbers alone are taken which are prime to it, and the number of pairs will be half the number of primes. The general theorem therefore is this:—If A be any number, prime or not, and m be the number of primes to it, which are 1,  $p, q, r, \&c.$ ; then  $1.p.q.r.\&c., \pm Z^{\frac{m}{2}}$  will be divisible by A, provided Z be prime to A, whether it be greater or less.

It follows from this that  $Z^{\frac{m}{2}} + 1$  must be divisible by A, and therefore that  $Z^m - 1$  must be divisible by A. If A be a prime number

and  $z$  a number prime to it (which every number not divisible by it is), this is Fermat's theorem, and the author has given a new proof of it. But the theorem is true though  $A$  be not a prime number, provided  $z$  be prime to  $A$  and  $m$  be the number of primes to  $A$ , and less than it; and instead of 1, any other number prime to  $A$  raised to the  $m$ th power may be substituted: and  $z^m - y^m$  will be divisible by  $A$ , provided  $z$  and  $y$  be primes to  $A$ , and  $m$  be the number of primes to  $A$  and less than it.

The author has therefore in this paper offered a proof of Gauss's theorem, and proved that it applies in certain cases to one half of the primes, and in all cases, with certain modifications, has shown that a similar property belongs to the product of the odd numbers, and also of the even numbers which precede any prime number; and lastly, has shown the intimate connexion between Wilson's theorem and Fermat's, and shown that each is but a part of a much more general proposition, which, he observes, may itself turn out to be part only of a still more universal one.

In a postscript, the author has shown that the well-known law of reciprocity of prime numbers is an immediate corollary from his theorem; and that it may be extended thus: if  $A$  and  $B$  be any two numbers (not prime numbers but) prime to each other, and the primes to  $A$ , and less than it, are ( $m$ ) in number, and the similar primes to  $B$  are ( $n$ ), then  $(A^n - 1)$  is divisible by  $B$ , and  $(B^m - 1)$  is divisible by  $A$ .

"On the reabsorption of the Mixed Gases in a Voltameter." By Professor M. H. Jacobi, in a letter to Michael Faraday, Esq., F.R.S. Communicated by Dr. Faraday.

The author found that if the mixed gases developed from the decomposition of water by a voltaic current, be allowed to remain in the voltameter in which they were collected, in contact with the fluid which produced them, they by degrees diminish in volume, and ultimately disappear by being absorbed by the fluid. He has not yet fully determined the precise conditions on which this phenomenon depends; but he is inclined to think that it is owing to a portion of the mixed gases, diffused throughout the whole liquid, coming into contact with the platinum plates, and being recombined on the surface of those plates; and this process being renewed with every fresh portion of the gases which takes the place of the former, the whole of the gases are thus reconverted into water.

March 4.—"Researches into the effects of certain Physical and Chemical Agents on the Nervous System." By Marshall Hall, M.D., F.R.S., &c.

The professed object of the author, in the present paper, is "to detail the results of an investigation of the phenomena and the laws of production and action of certain secondary or induced conditions of the nervous system, which are effected by a voltaic, and probably by any other electric current, but persistent after the influence of that current is withdrawn." This condition he designates by the new term *electrogenic*, as describing at once the origin and the independence of that condition. On the present occasion he confines

himself to the subject of the electrogenic condition of the muscular nerves, postponing to future inquiries that of the incident nerves and of the spinal marrow; and also the modes of action of other physical and chemical agents, such as mechanical injury, heat and cold, strychnine, and the hydrocyanic acid.

The bones and muscles of the brachial lumbar and pelvic regions of a frog, being isolated from all the other parts of the body, excepting only by means of their respective brachial and lumbar nerves, which were perfectly denuded on all sides, and raised from the glass on which the limbs were laid, a voltaic current from a pair of the "couronne de tasses" was passed downwards through the nerves, in a direction from their origin in the spinal marrow towards their terminations in the muscles. Energetic muscular movements were at first excited; and the current was thus continued during the space of five, ten, or fifteen minutes, and at the end of this period was withdrawn. No sooner was the current discontinued than the muscles were affected with spasmodic contractions, and with a tetanoid rigidity, constituting the secondary, or what the author denominates the *electrogenic condition*; an effect, which as instantly subsides on the restoration of the voltaic current.

The author proceeds to state the precautions which must be taken to ensure the success of experiments on this subject; and traces the effects of desiccation of the nerves from spontaneous evaporation, and of the application of external moisture, on the phenomena; and also the modifications introduced by varying the extent of voltaic contact. Various experiments are then described, which the author instituted with a view to ascertain the nature of the electrogenic condition of the nerves, and the circumstances under which it is induced; and he is led to the conclusion that the phenomena involve some voltaic principle which has not hitherto been fully investigated.

March 11.—"On the cause of the discrepancies observed by Mr. Baily with the Cavendish Apparatus for determining the Mean Density of the Earth." By George Whitehurst Hearn, Esq., of the Royal Military College, Sandhurst. Communicated by Sir John F. W. Herschel, Bart., F.R.S.

After taking a summary review of the methods employed by Mr. Baily for determining, on the plan devised by Mr. Cavendish, the mean density of the earth, and of the anomalies, hitherto unaccounted for, which had introduced perplexity in the results obtained, the author, suspecting that these anomalies had their source in the variable magnetic states of the masses which were the subject of experiment, traces the effects which such an influence might be supposed to have on those results. He finds that, the attraction arising from gravitation between a mass and one of the balls being exceedingly minute, an almost inconceivably feeble magnetic state may be the cause of great perturbations. He then proceeds to investigate the subject by the application of mathematical analysis; from which he is led to the conclusion that the masses and balls do actually exert on one another influences which are independent of the action of gravitation. He finds that such influences are of a

very fluctuating nature ; the action arising from them being either positive or negative, and its sign also changing in each revolution as the masses are turned round a vertical axis ; and he observes that such action may either fall short of that arising from gravitation or exceed it many times. Such disturbing force he conceives can be no other than a magnetic influence ; not however one of the ordinary kind, but that which Faraday has recently discovered as affecting all diamagnetic bodies.

The author concludes by proposing methods by which the inquiry should in future be conducted, so as to obviate or eliminate this source of error. Such an inquiry, he remarks, would, by exhibiting the magnetic and diamagnetic powers under new aspects, lead, in all probability, to important consequences.

March 18.—“Researches to determine the Number of Species and the Mode of Development of the British Triton.” By J. Higginbottom, Esq., F.R.C.S. Communicated by Thomas Bell, Esq., F.R.S.

The observations of the author, of which he gives a detailed account in the present memoir, have led him to the following conclusions :—

Two species only of the genus Triton are met with in England ; namely, the *Triton verrucosus* and the *Lisso-triton punctatus*. It is three years before the animal is capable of propagating its species, and four years before it attains its full growth. In its tadpole state, it remains in the water till its legs acquire sufficient strength to qualify it for progressive motion on land. While a land animal, it is in an active state during the summer, and passes the winter in a state of hibernation ; but does not then, as has been erroneously supposed, remain at the bottom of pools. Very dry, or very wet situations are incompatible with the preservation of life during the period of hibernation. At the expiration of the third year, the triton revisits the water, in the spring season, for the purposes of reproduction, and again leaves it at the commencement of autumn. Impregnation is accomplished through the medium of water, and not by actual contact. The growth and development of the triton are materially influenced by temperature, and but little by the action of light. The triton possesses the power of reproducing its lost limbs, provided the temperature be within the limits of 58° and 75° Fahrenheit ; but at lower temperatures, and during the winter, it has no such power.

April 15.—“On the Proper Motion of the Solar System.” By Thomas Galloway, Esq., A.M., F.R.S.

The object of this paper is to communicate the results of a calculation for determining the direction of the proper motion of the solar system from the apparent proper motions of stars in the southern hemisphere, deduced mostly from a comparison of the observations made by Lacaille at the Cape, about the middle of the last century, with the recent observations of Mr. Johnson and the late Professor Henderson at St. Helena and the Cape respectively. After advertizing to the papers of Sir William Herschel in the Philo-

sophical Transactions for 1783 and 1805, and some other investigations of the same subject, the author remarks that up to a recent period astronomers seem generally to have entertained the opinion that our knowledge of the proper motions of the stars is not sufficiently advanced to enable us to pronounce positively either on the fact or the direction of the motion of our own system. This opinion was grounded on the discrepancies which present themselves when it is attempted to explain the observed displacements of individual stars by referring them to the motion of the sun in an opposite direction; it being always found that whatever direction is assigned to the sun's motion, there are many stars whose proper motions cannot thereby be accounted for. But if the sun be in motion it is very improbable that any star is absolutely at rest; hence the proper motions deduced from a comparison of catalogues must be regarded as the effect partly of the true proper motions of the stars, and partly of the apparent systematic or parallactic motion caused by the displacement of the point of view; and as we have no reason for supposing the true proper motion of a star to be more probable in one direction than in another, it may be expected, *a priori*, that the observed directions will form angles of all different values with the direction of the sun's motion, or any other fixed line. The observed discrepancies are therefore not incompatible with a general drifting of the stars towards a particular region of the heavens; but in order to deduce the direction of the systematic motion, it becomes necessary to take account of a very considerable number of proper motions, and to represent them by equations, involving the unknown quantities required for determining the direction of the sun's motion, and to solve the equations so as to obtain the most probable values of those quantities. The first person who investigated the subject under this point of view was Professor Argelander of Bonn, in a paper published in the Petersburg Mémoirs for 1837. From the proper motions of 390 stars deduced from a comparison of Bessel's catalogue of Bradley's observations with his own catalogue of stars observed at Abo, Argelander found the direction of the sun's motion, for 1792·5, to be towards the point of the sphere whose right ascension is  $259^{\circ} 47' 6''$  and declination  $+32^{\circ} 29' 5''$ . Lundahl, subsequently, from a comparison of the places of 147 stars in the catalogues of Bessel and Pond, and not included among those considered by Argelander, found the co-ordinates of the point to be  $\text{R.A.}=252^{\circ} 24' 4'', \text{Dec. } +14^{\circ} 26' 1''$ ; and Otto Struve, still more recently, from the comparison of about 400 of Bradley's stars with the positions determined at the Dorpat Observatory, obtained the result  $\text{R.A.}=261^{\circ} 23' 1'', \text{Dec. } +37^{\circ} 35' 7''$ . The mean of those results taken with respect to their probable errors, was found by O. Struve to be  $\text{R.A.}=259^{\circ} 9' 4'', \text{Dec. } +34^{\circ} 36' 5''$ .

All the stars included in the calculations of Argelander, Lundahl, and O. Struve being situated to the north of the tropic of Capricorn, it appeared to be a point of some interest to determine whether the southern stars agree with the northern in their indication of the direction of the solar motion, or afford any confirmation of

the hypothesis of the sun's translation. Unfortunately, we have no observations made in the southern hemisphere in the last century equal in precision to those of Bradley, but the catalogue given by Lacaille in his 'Astronomiae Fundamenta,' furnishes a means of comparison of considerable value in reference to the present inquiry. In Mr. Johnson's 'Catalogue of 606 Stars in the Southern Hemisphere' (London, 1835), there are sixty-one which, on comparing their places in 1830 with those of Lacaille reduced to the same epoch, appear to have shifted their positions not less than 8" in space in the interval of eighty years between the epochs of the catalogues, or to have an annual proper motion of not less than one-tenth of a second in space. Prof. Henderson's catalogue (Mem. R. Astron. Society, vols. x. and xv.) furnishes thirty-six stars, which, on a like comparison, appear to have an annual proper motion exceeding the same limit. Of these, however, thirty-two are contained in Mr. Johnson's catalogue, but Henderson gives the proper motions of sixteen other stars (in the southern hemisphere), from the comparison of his own places with those of Bradley. On the whole, therefore, the two catalogues furnish eighty-one different stars whose proper motions are given both in right ascension and declination. The method of investigation is the same as that of Argelander. From the differences of  $\text{R.A.}$  and Dec. given by comparison of the catalogues, the direction of the *apparent* motion of each star is computed. It is then assumed that the sun is moving towards a point whose right ascension  $A=259^{\circ} 46' 2''$  and declination  $D=+32^{\circ} 29' 6''$ ; and the direction in which each star would appear to move, if it were itself at rest, is computed on this hypothesis. The difference of these two directions is treated as an error of observation, and its numerical value substituted for the differential of the angle which determines the direction of the parallactic motion; this differential being expressed by a formula containing the differentials of  $A$  and  $D$  multiplied by known coefficients. An equation is thus obtained of the form

$$0 = adA + bdD + n,$$

in which  $a$ ,  $b$ , and  $n$  are known quantities. Each star furnishes a similar equation; and the equations, being first multiplied respectively by the sine of the star's distance from the point assumed as the apex of the sun's motion, in order to give them all the same weight, are solved by the method of least squares, and the resulting values of  $dA$  and  $dD$  applied as corrections to the assumed values of  $A$  and  $D$ . The results are as follows:—the whole of the eighty-one equations give (for 1790) as co-ordinates of the point towards which the sun's motion is directed,

$$\text{R.A.} = 263^{\circ} 38' 0'' \pm 5^{\circ} 14' 5'' ; \text{Dec.} = +37^{\circ} 15' 0'' \pm 6^{\circ} 17' 6''.$$

But two of the stars compared with Lacaille move in a direction so nearly opposite to that of their motion on the assumed hypothesis, that (in one case especially) a slight error of observation would change the sign of  $n$  in the equations of condition. It therefore appears necessary to reject those two stars; and a further reason

for rejecting them is, that they are both situated within  $8^{\circ}$  of the pole, in which position Lacaille's determination of the right ascension is probably not to be depended upon. Setting aside, therefore, the two stars in question, the remaining seventy-nine equations give

$$R=256^{\circ} 51' 5 \pm 4^{\circ} 45' 1; \text{ Dec.} = +34^{\circ} 14' 3 \pm 5^{\circ} 36' 2.$$

The author further observes, that one of the stars compared with Bradley's catalogue is also remarkable as appearing to move in a direction nearly opposite to the mean direction of the whole, and that if this star be rejected also on account of the great probability there is that the parallactic motion is in this case concealed by the larger proper motion of the star itself in an opposite direction, the co-ordinates of the solar apex become

$$R=259^{\circ} 47' 4 \pm 4^{\circ} 31' 9; \text{ Dec.} = +34^{\circ} 19' 5 \pm 5^{\circ} 17' 7,$$

a result differing less than a degree either in right ascension or declination from the mean, as above stated, of the three previous determinations.

### XIII. Intelligence and Miscellaneous Articles.

#### ACTION OF CHLORINE ON ALCOHOL.—FORMATION OF ACETAL.

**M.** STAS states that he has observed that the causes which give rise to acetal are not always oxidizing causes. When chlorine is made to act upon alcohol, acetal is the principal product, as long as it does not act by substitution, and it is at once a dehydrogenating and an oxidizing body. This discovery, the author is of opinion, throws great light on the hitherto obscure action of chlorine upon alcohol.

In order to obtain acetal by the action of chlorine upon alcohol, it is sufficient to pass a current of chlorine into alcohol of 80 per cent., cooled to  $50^{\circ}$  or  $60^{\circ}$  F. The action is to be discontinued when chlorinated bodies commence formation by substitution : this is readily ascertained, for the alcohol then becomes turbid on the addition of water ; the liquid, which has become very acid, is to be distilled, and one-fourth of the quantity is to be preserved. This is to be neutralized by means of chalk, and by a fresh distillation one-fourth of the product is again to be obtained ; in this fused chloride of calcium is to be dissolved, which immediately separates a large quantity of a very volatile fluid, containing, like common rough acetal, aldehyd, acetic æther and alcohol ; by the addition of more chloride of calcium, the utmost quantity of alcohol and acetic æther are separated ; the purification of the acetal is to be completed.

The analysis of the acetal thus obtained was similar to that procured in the usual way ; and thus the chlorine acts, as already stated, both as a dehydrogenating and oxidizing body :  $C^{12}H^{18}O^6 + 2Ch - 2HO = C^{12}H^{14}O^4 + 2CH + 2HO$ .—*Ann. de Chim. et de Phys.*, Feb. 1847.

**BISILICATE OF IRON OR FERRUGINOUS PYROXENE.**

This new mineral is described in a memoir presented by M. Dufrénoy to the Academy in the name of M. Gruner, mining engineer, and Professor in the School of Mines at St. Etienne. It corresponds in composition to a pyroxene with a base of iron.

M. Gruner states that this mineral resembles certain varieties of asbestos, or more nearly fibrous amphibole. Its specific gravity is 3·713, which exceeds that of the densest epidotes, amphiboles or pyroxenes. By analysis M. Gruner obtained—

Silica .....	43·9
Protoxide of iron .....	52·2
Lime .....	.5
Magnesia .....	1·1
Alumina.....	1·9
	<hr/>
	99·6

Admitting that the greater portion of the foreign bases is derived from a small quantity of the gangue, it will be seen that this mineral is bisilicate of iron, or ferruginous pyroxene with one base only.—*Comptes Rendus*, Mai 5, 1847.

**CHLOROSULPHURET OF SILICUM.**

M. Isidore Pierre states that when hydrosulphuric acid and chloride of silicum in vapour are passed through a porcelain tube heated to redness, they react upon each other: much hydrochloric acid is produced, which is disengaged with excess of hydrosulphuric acid gas and a little chloride of silicum, which escapes the reaction.

If the products of this reaction be passed into a U-shaped tube immersed in cold water, a fuming liquor condenses, which has a sharp foetid odour, resembling that of hydrosulphuric acid and chloride of sulphur. The liquor thus obtained was slightly opaque by sulphur suspended in it: this was deposited by being left forty-eight hours in a well-stoppered bottle. There were also deposited on the sides of the bottle, clear lemon-yellow crystals, which were sulphur in the form of oblique rhombic prisms, without any modification.

The condensed liquor has consequently the power of dissolving sulphur, and of depositing it in crystals belonging to the same system as those which are obtained in the dry way. The smallness of these crystals prevented the author from determining their angles; but he reckons upon being able soon to do so. No sensible traces of sulphuret of silicum were found in the minute deposit produced in the porcelain tube.

The liquid condensed in this operation was distilled in an oil-bath from a retort furnished with a thermometer: the more volatile portions, which usually distil from 140° to 176° F., were rejected. They consist principally of chloride of silicum mixed with a small quantity of chlorosulphuret. Afterwards there is obtained a limpid colourless liquid which fumes in the air, and has an odour resembling that of chloride of silicum and hydrosulphuric acid.

Its specific gravity at 60° F. is about 1·45 ; that is, a little less than that of chloride of silicium. When it is thrown into water, it occasions an abundant disengagement of sulphuretted hydrogen gas and a slight deposit of sulphur. It boils at above 212° F. ; but the small quantity obtained did not allow of ascertaining its exact boiling-point.

By analysis, it yielded such proportions of its constituents as to indicate for its formula  $\text{Cl}_2 \text{S Si}$ , which would give—

Chlorine .....	65·47
Sulphur.....	14·83
Silicium.....	19·70
	100·00

M. Pierre proposes the name of *chlorosulphuret of silicium* for this compound.—*Ibid*, Mai 5, 1847.

#### METEOROLOGICAL OBSERVATIONS FOR MAY 1847.

*Chiswick*.—May 1. Very fine. 2. Cloudy. 3. Rain. 4. Cloudy. 5. Cloudy and fine. 6. Slight fog : fine. 7. Overcast: showery. 8. Rain. 9. Fine : cloudy : densely overcast : rain. 10. Very fine : slight showers. 11. Cloudy. 12. Very fine. 13. Cloudy and fine : showers. 14. Showery. 15. Fine : rain at night. 16. Rain : cloudy : rain at night. 17. Cloudy. 18. Fine : rain. 19, 20. Cloudy and fine. 21, 22. Very fine. 23. Very hot and sultry. 24. Cloudy and fine. 25—27. Very fine. 28. Slight haze : sultry. 29. Cloudy : thunder and heavy rain. 30. Clear and fine. 31. Cloudless : exceedingly fine.

Mean temperature of the month ..... 56°·83

Mean temperature of May 1846 ..... 56°·16

Mean temperature of May for the last twenty years ... 55°·01

Average amount of rain in May ..... 1·84 inch.

*Boston*.—May 1. Fine. 2. Cloudy : rain early A.M. : rain P.M. 3. Cloudy : rain A.M. and P.M. 4. Cloudy. 5. Fine : rain P.M. 6. Cloudy. 7. Fine : rain P.M. 8. Cloudy : rain P.M. 9. Cloudy. 10. Cloudy : rain early A.M. 11. Rain. 12. Fine : rain, with thunder P.M. 13. Fine : rain P.M. 14, 15. Fine : rain early A.M. 16. Rain : rain, with thunder P.M. 17. Cloudy. 18. Cloudy : rain P.M. 19, 20. Cloudy. 21—24. Fine. 25. Windy. 26, 27. Fine. 28. Fine : 1 o'clock P.M., thermometer 82°. 29. Rain : 4 o'clock A.M. thunder, hail and rain : rain all night. 30. Fine : rain early A.M. 31. Fine.

*Sandwick Manse, Orkney*.—May 1. Bright : clear. 2. Bright : drops. 3. Bright : clear. 4. Bright : damp. 5. Fine. 6, 7. Cloudy : damp. 8, 9. Drizzle : fog. 10. Clear : fine. 11. Cloudy : rain. 12. Rain : cloudy. 13. Cloudy. 14. Rain : fog. 15. Damp : rain : fog. 16. Bright : cloudy. 17, 18. Cloudy : clear. 19. Showers : drizzle. 20. Fog : cloudy. 21. Bright : rain. 22. Showers. 23. Clear. 24. Fine. 25. Bright : cloudy. 26. Bright : showers. 27. Fine : clear. 28. Fine : cloudy : fine. 29. Rain : thunder : cloudy : fine. 30. Clear : fine. 31. Cloudy : fine.

*Applegarth Manse, Dumfries-shire*.—May 1. Fine summer day. 2. Mild : showers. 3. Cloudy : keen. 4. Spring, but keen. 5. Cold : wet P.M. 6. Growing : wet P.M. 7. Dull : showers. 8. Dull : wet P.M. 9. Mild : dull : wet P.M. 10. Fine growing day. 11—14. Dull : showers. 15. Fine summer day. 16. Stormy : wet all day. 17. Wet and cold. 18. Wet and stormy. 19. Dull : wet. 20. Sunshine : fine. 21. Dry : cloudy. 22. Cloudy : showers. 23. Warm : thunder : rain. 24. Fine : clear : wet P.M. 25. High wind : clear. 26. Fine : clear : light : cloudy. 27. Fine : clear : thunder. 28. Fine : wet P.M. 29. Fine : heavy rain P.M. 30. Fine : warm. 31. Remarkably fine.

Mean temperature of the month ..... 51°·1

Mean temperature of May 1846 ..... 52°·6

Mean temperature of May for twenty-five years ..... 51°·1

Mean rain in May for twenty years ..... 1·69 inch.



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[THIRD SERIES.]

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AUGUST 1847.

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XIV. *On a new Voltaic Battery, cheap in its construction and use, and more powerful than any Battery yet made; and on a cheap substitute for the nitric acid of Grove's Platina Battery.* By the Rev. N. J. CALLAN, Professor of Natural Philosophy in the Royal College, Maynooth\*.

SOME time ago, whilst I was reflecting on the principle of action of Grove's and Bunsen's batteries, it occurred to me that lead might be substituted for the platina of the former and the carbon of the latter. I put into the porous cell of a Grove's battery a piece of lead about  $\frac{1}{16}$ th of an inch thick, two inches broad and six inches long. I found that the voltaic current produced by the lead excited by a mixture of concentrated nitric and sulphuric acid was very powerful. I afterwards compared the power of this leaden battery with that of a platina one of the same size, by sending through the helix of a galvanometer, at the same time, but in opposite directions, the currents produced by the two batteries. Both batteries were charged with the same acids; the lead and platina were excited by concentrated nitric and sulphuric acid, and the zinc by dilute sulphuric acid. The current from the platina battery destroyed the deflection produced by the leaden one, and caused an opposite deflection, which indicated that the former current was about twice as strong as the latter. The two batteries were left working for about three hours and a half. At the end of that time the current from the lead was about twice and a half as powerful as the current from the platina. The quantity of lead dissolved during these three hours and a half was very small.

It struck me that by diminishing the action of the acids on the lead, I might increase the power of the battery. I therefore covered a leaden plate with gold leaf, and coated another

\* Communicated by the Author.

of the same size with chloride of gold, in the same way in which sheet silver is platinized for Smee's battery. These plates and a platina one of the same size were put successively into the porous cell of a Grove's battery, and the voltaic current sent through the helix of our large electro-magnet, in which the iron bar is about thirteen feet long and two and a half inches thick; the copper wire is about 500 feet long and one-sixth of an inch diameter. The magnetic power given to the electro-magnet by the leaden plate coated with chloride of gold, appeared to be equal to that which was produced by the platina plate. The magnetic effect of the current from the leaden plate covered with gold leaf was not so great. A coating of chloride of platina was afterwards found to answer as well as one of chloride of gold.

Some days after a leaden and platina battery of the same size were left working for four hours and a half. At the end of that time the lead plate acted fully as well as the platina. When the nitric acid was so much exhausted that the lead was barely capable of magnetizing the large electro-magnet so as to make it sustain a certain weight, the leaden plate was taken out of the porous cell, and a platina plate of the same size put in its stead. The platina plate was not able to make the electro-magnet sustain the weight which the lead had caused it to sustain.

The magnetizing power of the platinized or gilded lead and platina batteries was compared several times in working an electro-magnetic machine. On these occasions the power of the leaden battery was evidently superior to that of the platina one. Sometimes the platina plate was taken out of the porous cell, and a platinized or gilded lead plate of the same size put in its place: the velocity of the machine was instantly and considerably increased. The same effect was produced when the platina plate was taken out of the cell and a platinized platina one put in its stead. Hence it appears that a leaden plate coated with chloride of platina or gold, or a platinized platina plate, produces a more powerful voltaic current than a platina plate does. On the 24th of last May, a small platinized lead battery and a Grove's battery of the same size, were exhibited before the Royal Irish Academy. The power of the former was obviously superior to that of the latter. By using double leads and single zincs instead of double zincs and single leads, the power of the battery appears to be increased. When the lead plates have been used for a long time, they require to be newly gilded or platinized. After being used they should be rinsed in water, and dipped into a weak solution of chloride of gold or platina.

Seeing that the concentrated acids, by dissolving the lead, removed the gold or platina powder, and that the nitric acid was very expensive, I endeavoured to find in its stead a cheap substitute which would not act on the lead. The first that occurred to me was common nitre. I dissolved about the eighth of an ounce of it in sulphuric acid, which I diluted with nearly an equal bulk of water. I poured the mixture into the porous cell of a Grove's battery, and put into it a platinized leaden plate. I then sent the voltaic current through the helix of our large electro-magnet: the magnetic power given to the magnet appeared to be greater than that which was given to it by a Grove's battery of the same size, in which the platina was excited by concentrated nitric and sulphuric acid. I afterwards compared the heating power of the two batteries, and found the power of the platinized lead battery to be evidently superior to that of the other. I charged a platinized leaden battery with a mixture consisting of about five parts of sulphuric acid, five of solution of nitre, and one of nitric acid, and a Grove's battery with equal parts of nitric and sulphuric acid. The former fused a piece of steel wire which the latter only raised to a white heat. When a platina plate is excited by a mixture of sulphuric acid and a solution of nitre, the voltaic current appears to be as powerful as that which is produced by the plate when excited by concentrated nitric and sulphuric acid. The cost of the nitre necessary for charging a battery is about the twentieth part of that of the nitric acid. The power of the former declines sooner than that of the latter: but from the results of several experiments, I have come to the conclusion that the expense of doing a given amount of work by a platina battery excited by concentrated nitric and sulphuric acid, would be three or four times as great as if the work were done by a platinized lead battery excited by a mixture of sulphuric acid and a solution of saltpetre. I have tried nitrate of soda, or cubic nitre, and nitrate of ammonia, as substitutes for nitric acid; but although they give great power, they do not answer as well as the common nitre. A solution of common nitre and cubic nitre along with sulphuric acid, forms a mixture scarcely inferior to the solution of common nitre and sulphuric acid. The most powerful mixture for the platina or platinized lead battery consists of about four parts of sulphuric acid, two of nitric acid, and two of a saturated solution of nitre. When no nitric acid is used, at least one half of the mixture should consist of sulphuric acid, and the remainder of nitre and water: the solution need not be saturated with nitre. Four parts of sulphuric acid, two of a solution of chromate of potash, and two

of the solution of nitre, make a most powerful exciting mixture for platina, but give comparatively little power to platinized lead. I endeavoured to find among the sulphates a substitute for sulphuric acid, but did not succeed. The voltaic current from a platinized lead battery, excited by two parts of sulphuric acid, three of sulphate of soda, and three of nitrate of potash, is very powerful, but considerably inferior to that which is produced by the concentrated acids.

On finding that platinized or gilded lead and platinized platina were superior to platina, I saw that the cause of the superiority was that, in the platinized or gilded lead, and in the platinized platina batteries, the acting metals were, not lead or platina and zinc, but gold or platina powder, and zinc; and that the gold or platina powder was more negative compared with zinc than platina is. Hence I inferred, first, that a leaden plate coated with any of those substances which are more negative and cheaper than platina or gold, would act as powerfully as platinized or gilded lead; and secondly, that any other metal to which the platina or gold powder would adhere might answer as well as lead. I therefore coated, by the galvanic process, leaden plates with antimony, arsenic, chromium, molybdenum and borax. The plates coated with arsenic and molybdenum were much inferior to platina: those that were coated with antimony and borax appeared fully equal to platinized lead, but they soon lost their power. The first plate which I chromed acted as well, and retained its power nearly as long as platinized or gilded lead. I afterwards coated a great number of plates with chromium; but all of them were far inferior to the first. The power of a leaden plate is greatly increased by being coated with mercury, or even with clay boiled in aqua regia, or with any other substance which I tried; but I have not found any substance to answer as well as the chloride of gold or platina.

I have compared with platinized lead, the other cheap metals coated with gold or platina, or chromium; and with the exception of cast iron, they were all inferior to it. Platinized or chromed cast iron answers as well as platinized lead; and without being chromed or platinized, cast iron appears to act as powerfully as platina. The power of a cast iron battery in magnetizing our large electro-magnet, and in driving an electro-magnetic machine, was compared with that of a Grove's battery of the same size. In the two batteries the exciting mixture was the same. The power of the former appeared to be fully equal to that of the latter.

From the results of several experiments which I have made on the relative power of platinized silver and platinized lead,

I feel confident that the latter may, without any diminution of power, be substituted for the former in Smee's battery. Cast iron does not take the coating of platina powder (at least until the hard surface is worn away) so well as lead or silver, and on that account it does not act as powerfully as either. But I have found zinc and cast iron excited by dilute sulphuric acid as constant in their action as zinc and platinized lead. A platinized lead, or cast iron plate six inches square, may be had for the twelfth part of the cost of a platinized sheet of silver of the same size.

From the experiments which have been described, I infer, first, that a battery superior in power to Professor Grove's nitric acid battery may be made by substituting platinized platina or lead for platina, and nitrosulphuric acid and nitrate of potash for nitric and sulphuric acid; and secondly, that a battery equal in power to the nitric acid battery may be constructed by the substitution of cast iron for platina.

The advantage of what I may call the nitre platina battery over the nitric acid one is, that the expense of working the former is, as has been already stated, considerably less than that of working the latter.

The advantage of the cast iron or platinized leaden batteries over Professor Grove's is, that they are far less expensive in their construction. A plate of cast iron or platinized lead may be had for a shilling, whilst a platina plate of the same size will cost nearly three pounds. Besides, a cast iron or platinized lead battery may be worked by a mixture of nitre and sulphuric acid for one hour for about the tenth part of the expense of working a Grove's battery for the same time.

The cheapness of cast iron and platinized lead will enable every one to procure a powerful voltaic battery. A platinized lead battery is about fifteen times as powerful as a common Wollaston battery of the same size. A cast iron battery is a little less powerful than the platinized lead one; but I prefer the former, because the cast iron does not require to be chromed or platinized. I am now preparing two large cast iron batteries for the College: one will contain about thirty-three square feet of zinc and sixty-six of cast iron, the other will contain eighty square feet of zinc and a hundred and sixty of cast iron. These batteries will be more powerful than any battery ever constructed. The expense will be very moderate; for the zinc plates and Wedgwood troughs of our former batteries will answer for the new ones.

Maynooth College, July 3, 1847.

XV. *On the Perturbations of Planets moving in Eccentric and Inclined Orbits.* By Sir J. LUBBOCK, Bart., F.R.S.

[Continued from page 6.]

**I**N the last Number of the Philosophical Magazine I described tables by which the development of the disturbing function  $R$  is greatly facilitated. I shall now describe other tables which have been calculated for me by Mr. Farley, and which also facilitate the numerical solution. The advantages which the employment of tables presents wherever they can be applied are well known. Not only the march of the figures affords security against error, but the computer acquires facility in such calculations systematically undertaken, while the operations are more easy than they would be if the quantities required were not connected by a common origin, or so troublesome as they would be if undertaken by different individuals, or by the same individual at different times. The use of tables is out of the question in a literal or algebraic development; but, on the contrary, it is an important property of the numerical development that it can thus be materially facilitated.

All developments whatever may be resolved into three classes, which I call *literal*, *quasi-literal*, and *arithmetic*. *Literal* or *algebraical* are those which result when the numerical values of the constants are inserted last, and after the development is complete. *Quasi-literal* are those which result when either a part only of the constants are expressed by means of general symbols, or when the development is made up of several distinct processes, and when the numerical values are inserted after a portion of these, but not all have been accomplished. Finally, *arithmetic* or *numerical* developments are those which result when the numerical values of the constants are inserted in place of the general symbols before any step of the development is attempted.

A *literal* development is generally preferable, for this reason, that if it can be performed, the development which results serves for every possible value which can be assigned to the constants. Such, for instance, is the development of the disturbing function due to M. Binet; and if such a development in terms of the requisite variables could be accomplished and carried out to a sufficient extent, and if, being accomplished, numerical values of the constants could be easily introduced, it would be preferable to any other. M. Hansen's development, in his Memoir on the Perturbations of Encke's Comet by Saturn, is a *quasi-literal* development, because a portion only of the processes is general. The conversion of the quan-

tities  $P_{k,i}$  into explicit functions of sines and cosines of multiples of  $f$  is an *arithmetical* process; while the calculation of the quantities  $A_{n,i}$  in p. 29 of M. Hansen's paper, is literal or algebraical.

I regard as very difficult any development of the disturbing function, either *literal* or *quasi-literal*, when the eccentricity of the disturbed body is considerable and the perturbations are large, as in the case of Encke's comet disturbed by Jupiter; and if such were possible, the replacement of the numerous symbols by numbers at the conclusion, would be an operation of almost insurmountable difficulty. On the other hand, in performing an *arithmetical* development according to the rules which I have invented, not only no quantity can be introduced which has a numerical value beneath any given limit (say beneath unity in a given decimal place), but it is equally impossible, except by a numerical mistake, that any quantity which is above that limit can be omitted. The developments may also be effected by mechanical quadratures, as explained by M. de Pontécoulant (*Théor. Anal.*, vol. iii.), or by the method given by M. Le Verrier in the first number of the *Développements sur plusieurs points de la Théorie des Perturbations des Planètes*.

If  $x, y, z$  are rectangular co-ordinates of a comet or planet  $m$ , and  $f$  the true anomaly,

$$x = r\{V \cos f + Q \sin f\},$$

$$y = r\{O \cos f + A \sin f\},$$

$$z = r\{X \cos f + Y \sin f\}.$$

\* $V, Q, O, A, X, Y$  are constants which depend only on the elliptic constants of the planet  $m$ , and such that

$$V = \cos \pi + 2 \sin^2 \frac{\iota}{2} \sin(\pi - \nu) \sin \nu,$$

$$Q = -\sin \pi + 2 \sin^2 \frac{\iota}{2} \cos(\pi - \nu) \cos \nu,$$

$$O = \sin \pi - 2 \sin^2 \frac{\iota}{2} \sin(\pi - \nu) \cos \nu,$$

$$A = \cos \pi - 2 \sin^2 \frac{\iota}{2} \cos(\pi - \nu) \cos \nu,$$

$$X = \sin(\pi - \nu) \sin \iota,$$

$$Y = \cos(\pi - \nu) \sin \iota.$$

\* I have had occasion to use so many alphabets in the course of the work from which this is extracted, that I have had recourse to this artifice of reversing the letters in order not to use the same symbol in two different significations.

Mr. Farley has calculated for me a table of the values of these quantities for all the planets, and also for the comet of Encke, the comet of Biela, and the comet of Halley.

$$\frac{aR}{\mu} = \frac{m' a'}{\mu r^j} \left\{ \sigma^2 \frac{a'}{r^j} \frac{r}{a} \cos \delta - \eta \{1 + P\}^{-\frac{1}{2}} \right\},$$

$$1 + P = 1 - \frac{2\eta^2}{\sigma} \left\{ \left\{ \mathfrak{A} \frac{r}{a} \cos f - \mathfrak{B} \frac{r}{a} \sin f \right\} \frac{a'}{r^j} \cos f' \right.$$

$$+ \left\{ \mathfrak{C} \frac{r}{a} \cos f + \mathfrak{D} \frac{r}{a} \sin f \right\} \frac{a'}{r^j} \sin f' \Big\}$$

$$+ \eta^2 \left\{ \frac{a'^2}{r^j} \frac{r^2}{a^2} - 1 \right\}.$$

$$\mathfrak{A} = \mathfrak{E}E + \mathfrak{F}F + \mathfrak{G}G + \mathfrak{H}H, \quad -\mathfrak{B} = \mathfrak{A}B + \mathfrak{C}D + \mathfrak{E}F + \mathfrak{G}H,$$

$$\mathfrak{C} = \mathfrak{E}A + \mathfrak{F}C + \mathfrak{G}B, \quad \mathfrak{D} = \mathfrak{B}B + \mathfrak{D}D + \mathfrak{F}F + \mathfrak{H}H.$$

I call the quantities  $\frac{a'}{r^j} \cos f'$ ,  $\frac{a'}{r^j} \sin f'$ ,  $\frac{r}{a} \cos f$ ,  $\frac{r}{a} \sin f$ ,  $\frac{r^2}{a^2}$ ,  $\frac{a'^2}{r^j^2}$ , &c. the *elementary quantities*, because they are the *elements* which, by means of various combinations, form the disturbing function  $R$ ,  $\frac{rdR}{dr}$ , &c., and if the numerical values of the constants are introduced before the development is begun are alone required.

Mr. Farley has calculated the coefficients of these quantities when they are developed in terms of the mean motions for the planets, and also other tables for eccentricity, .1, .2, . . . .7, which show the convergence to be so slight, that such mode of development can only be employed when the eccentricity is small. These tables have all been constructed by means of mechanical quadratures. These tables are not wanted for the comets, because their co-ordinates cannot be developed in terms of their mean anomalies in sufficiently converging series.

When the method of mechanical quadratures is applied to the determination of the perturbations of comets, a *correction* is required; but when that method is used for the determination of coefficients of this nature, the limits of the integral are 0 and  $360^\circ$ , and the correction vanishes; so that by means of several particular values, rigorous values of the coefficients are easily obtained. Nor does the width of the interval matter, provided it is not made too large. It is difficult to give precise rules to regulate the width that should be employed; but in the formation of these tables it was easy to employ various modes of verification. As this inquiry is in its infancy, I considered it sufficient to retain only those terms which are

due to the elliptic motion; but hereafter it may be desirable to reconstruct the tables of the *elementary quantities* for each of the planets, retaining some of the principal inequalities due to the disturbing force.

Pingré, in his work on comets many years since, gave a list of comets, with their elements. At that time, however, the method of finding the orbit, or even the distance of a comet, was understood by so few persons, that, from that and other causes, the numbers contained in that table may not be accurate: many other comets have been discovered since, and such a table brought up to the present time appears to be an important desideratum in astronomy.

Mr. Hind has kindly favoured me with the following list of comets which have been made out to be periodic:—

Elements of Halley's comet, by Westphalen, for 1835. *Ast. Nach.*, No. 588.

$$e = .96739 \quad \pi = 304^\circ 31' 32'' \cdot 19 \quad v = 55^\circ 9' 59'' \cdot 34 \\ i = 17^\circ 45' 5'' \cdot 13 \quad a = 17 \cdot 98791 \quad \text{Retrograde.}$$

Elements of Encke's comet by Encke, for 1829. *Ast. Nach.*, No. 489.

$$e = .84462 \quad \pi = 157^\circ 17' 53'' \cdot 35 \quad v = 334^\circ 29' 31'' \cdot 62 \\ i = 13^\circ 20' 34'' \cdot 49 \quad a = 2 \cdot 22391 \quad \text{Direct.}$$

Elements of Biela's comet, 1846, by Prof. Plantamour. *Ast. Nach.*, No. 584.

$$e = .75700 \quad \pi = 109^\circ 2' 20'' \cdot 10 \quad v = 245^\circ 54' 38'' \cdot 8 \\ i = 12^\circ 34' 53'' \cdot 47 \quad a = 3 \cdot 52452 \quad \text{Direct.}$$

Elements of the comet of Faye, by M. Le Verrier, for 1844, omitting the terms multiplied by  $\mu''$ . *Ast. Nach.*, No. 541.

$$e = .55596 \quad \pi = 49^\circ 34' 19'' \cdot 39 \quad v = 209^\circ 29' 19'' \cdot 26 \\ i = 11^\circ 22^\circ 31'' \cdot 40 \quad a = 3 \cdot 81179 \quad \text{Direct.}$$

Elements of DeVico's first comet, by Dr. Brünnow, for 1844. *Ast. Nach.*, No. 563.

$$e = .61765 \quad \pi = 342^\circ 30' 49'' \cdot 64 \quad v = 63^\circ 49' 0'' \cdot 11 \\ i = 2^\circ 54' 50'' \cdot 33 \quad a = 3 \cdot 10295 \quad \text{Direct.}$$

Elements of Brorsen's first comet, by Dr. Brünnow, for 1846. *Ast. Nach.*, No. 557.

$$e = .79362 \quad \pi = 116^\circ 28' 34'' \quad v = 102^\circ 39' 36'' \cdot 5 \\ i = 30^\circ 55' 6'' \cdot 6 \quad a = 3 \cdot 15021 \quad \text{Direct.}$$

The following are the elements of the comet of Encke for 1829 used by M. Hansen: Additions à la Conn. des Temps, 1847, p. 54.

$$e = .844676 \quad \pi = 157^\circ 18' 24'' \cdot 6 \quad v = 334^\circ 29' 28'' \cdot 8 \\ i = 13^\circ 20' 40'' \cdot 2 \quad a = 2 \cdot 21997.$$

*Ast. Nach.*, No. 541.

XVI. *On the Heat of Vapours.*  
By Sir J. LUBBOCK, Bart., F.R.S.\*

LET  $V$  be the quantity of absolute heat, considered as a function of the sensible heat or temperature  $\theta$ ,

$$\frac{dV}{d\theta} = \frac{dV}{d\rho} \frac{d\rho}{d\theta} + \frac{dV}{dp} \frac{dp}{d\theta} \quad p = k\rho(1 + \alpha\theta),$$

$\rho$  being the density,  $p$  the pressure,  $k$  and  $\alpha$  constants,

$$\frac{d\rho}{d\theta} = -\frac{\alpha\rho}{1 + \alpha\theta} \quad \frac{dp}{d\theta} = \frac{\alpha p}{1 + \alpha\theta}.$$

If  $c$  is the specific heat of a gas, the pressure being constant, and  $c_i$  its specific heat when the volume is constant, so that

$$c = \frac{dV}{d\rho} \frac{d\rho}{d\theta} \quad c_i = \frac{dV}{dp} \frac{dp}{d\theta} \quad \gamma = \frac{c}{c_i}$$

$$\rho \frac{dV}{d\rho} + \gamma p \frac{dV}{dp} = 0.$$

Laplace evidently considered  $\gamma$  constant, and he integrated this equation upon that hypothesis, "En supposant cette quantité rigoureusement constante, &c.", *Méc. Cél.* vol. v. p. 127. Again, Poisson, in repeating the same theory, *Traité de Méc.*, vol. ii. p. 646, "En regardant  $\gamma$  comme une quantité constante, &c." If  $\gamma$  is constant,

$$V = A + B \frac{p^{\frac{1}{\gamma}}}{\rho} = A + B \frac{k}{\alpha} \left( \frac{1}{\alpha} + \theta \right) p^{\frac{1}{\gamma}-1},$$

(see vol. xviii. p. 507) which is identical with the equation given in the *Comptes Rendus*, Séance de 31 Mai 1847, p. 920,

$$q = m + n(a + t)p^{-z},$$

$$m = A, \quad n = \frac{Bk}{\alpha}, \quad a = \frac{1}{\alpha}, \quad t = \theta, \quad z = 1 - \frac{1}{\gamma}, \quad k = \gamma;$$

but if, as Professor Holtzmann maintains (see Taylor's Scientific Memoirs, vol. iv. part 14),  $z$  is variable, the integral of Laplace does not necessarily obtain, nor does the equation (*Comptes Rendus*, p. 920)

$$\frac{dq}{dt} = np^{-z}$$

obtain; because if  $z$  is a function of  $t$ ,

$$\frac{dq}{dt} = np^{-z} - n(a + t)p^{-z} \log p \frac{dz}{dt},$$

\* Communicated by the Author.

and

$$q - q_1 = n(a + t)p^{-z} - n(a + t_1)p_1^{-z_1}.$$

It has not, I believe, been remarked, that the integral

$$V = A + B \frac{p^{\gamma}}{\rho^{\frac{1}{\gamma}}}$$

will however still satisfy the differential equation

$$\frac{\rho dV}{dp} + \gamma p \frac{dV}{dp} = 0.$$

If

$$\frac{1}{\rho} \frac{d\gamma}{dp} + \frac{1}{\gamma p} \frac{d\gamma}{dp} = 0$$

or

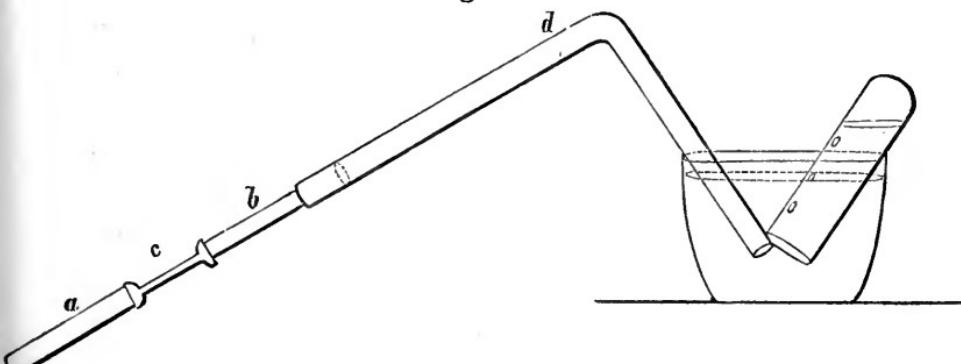
$$\gamma k(1 + \alpha \theta) \frac{d\gamma}{dp} = - \frac{d\gamma}{dp}.$$

*XVII. On certain Phænomena of Voltaic Ignition and the Decomposition of Water into its constituent Gases by Heat.*  
By W. R. GROVE, Esq., M.A., F.R.S.

[Continued from p. 35.]

I WAS now anxious to produce a continuous development of mixed gas from water subjected to heat alone, in other words, to succeed in an experiment which should bear the same relation to experiment fig. 9 as fig. 5 did to fig. 7; for this purpose the apparatus shown at fig. 10 was constructed: *a* and

Fig. 10.



*b* are two silver tubes 4 inches long by 0.3 inch diameter; they are joined by two platinum caps to a platinum tube *c*, formed of a wire one-eighth of an inch diameter drilled through its entire length, with a drill of the size of a large

pin; *a* is closed at the extremity, and to the extremity of *b* is fitted, by means of a coiled strip of bladder, the bent glass tube *d*. The whole is filled with prepared water, and having expelled the air from *a* by heat, the extremity of the glass tube is placed in a capsule of simmering water. Heat is now applied by a spirit-lamp, first to *b* and then to *a*, until the whole boils; as soon as ebullition takes place, the flame of an oxyhydrogen blowpipe is made to play upon the middle part of the platinum tube *c*, and when this has reached a high point of ignition, which should be as nearly the fusing-point of platinum as is practicable, gas is given off, which, mixed with steam, very soon fills the whole apparatus and bubbles up from the open extremity, either into the open air or into a gas collector. Although by the time I had devised this apparatus I was from my previous experiments tolerably well assured of its success, yet I experienced a feeling of great gratification when on applying a match to one of the bubbles which were ascending, it gave a sharp detonation; I collected and analysed some of it; it was 0·7 oxyhydrogen gas, the residue nitrogen, with a trace of oxygen.

Those who have endeavoured to deprive water of air, will have no difficulty in accounting for the residual nitrogen, or nitrogen mixed with a small portion of oxygen, which has occurred in all my experiments. De Luc pointed out the impossibility of practically depriving water of air, and Priestley, from observing the obstinacy with which water retained air, was led to believe that water was convertible into nitrogen (phlogisticated air). I have repeated several of Priestley's experiments under much more stringent circumstances, and have never been able to free water from air, or so to boil water that for every ebullition of vapour a minute bubble of permanent gas was not left, which appeared to have been an indispensable nucleus to the vapour.

The difficulty of boiling water increases, as M. Donny has proved, in proportion to its freedom from air, and at last the bursts of vapour become so enormous that the vessels employed are generally broken. There appears to me a point beyond which this resistance does not extend; but even at this point a minute bubble of air is left for each burst of vapour, though they are so few and distant that the aggregate amount of gas is very trifling. I have produced from water which had been previously carefully deprived of air by the ordinary methods, three-fourths of its own volume of permanent gas, which proved to be nitrogen; but as the water in this experiment was boiled under a long column of oil, it is probable that if any oxygen were present, it might have been

absorbed by the oil ; I have, however, always found the proportion of oxygen to decrease as the boiling was continued. It may be worth noticing, as having had some influence on my mind, that many months ago, when considering the experiments of Henry and Donny on the cohesion of water, I mentioned to Mr. Gassiot, and also to Mr. Bingham my assistant (to whose assiduity I am much indebted), that I was inclined to think if water could be absolutely deprived of air, it would be decomposed by heat, a result which I have now attained by a totally different series of inductions. It is a circumstance worthy of remark, that I find the greater part of the air to be expelled at a comparatively low temperature, and when the water has come in contact with the platinum, while the decomposition all takes place when the platinum is surrounded by an atmosphere of steam, if steam it may be called, for the state of this atmosphere at the first immersion of the platinum is at present very mysterious.

I think I may now safely regard it as proved, that platinum intensely ignited will decompose water, and several considerations press on the mind in reflecting on this novel phænomenon.

First of all, to those who are attached to the *cui bono* argument, and estimate physical science in proportion only to its practical applications, I would say that these experiments afford some promise of our being, at no distant period, able to produce mixed gases for purposes of illumination, &c. by simply boiling water and passing it through highly ignited platinum tubes, or by other methods which may be devised ; we in fact by this means, as it were, boil water into gas, and there appears theoretically no more simple way of producing chemical decomposition.

To pass however to more important considerations : the spheroidal state, which has lately attracted the attention of philosophers, appears to be closely connected with these results, and is rendered more deeply interesting. The last experiment but two which I have mentioned, shows that the spheroidal state is intermediate between ordinary ebullition and the decomposing ebullition ; it is probably therefore a state of polar tension, coordinate in some respects with that which takes place in the cell of a voltaic combination before decomposition, or when the power employed not being of sufficient intensity to produce actual decomposition, the state commonly called polarization of the electrodes, obtains. The phænomenon brings out also a new relation between heat, electricity, and chemical affinity ; nitherto many electrical phænomena could be produced by heat and chemical action,

the difference being that in the effects produced by the last two forces there was no polar chain, but every minute portion of the matter acted on gave rise to the phenomena which in the electrical effects are only observable at the polar extremities; thus in decomposing water by iron and sulphuric acid, or by passing steam over heated tubes of iron, parallel results are obtained to the electrolysis of water with an iron anode; but in the former cases every portion of the iron oxidated gives off its equivalent of hydrogen, in the latter the equivalent is evolved from the cathode at a point distant from that where the oxidation takes place. Hitherto electricity has been the only force by which many compounds, and particularly water, could be resolved into their constituents without either of these being absorbed by another affinity. The decomposition by ignited platinum removes this exception, and presents the parallel effect produced by heat alone.

Although there is no substance except platinum and some of the more rare metals, such as iridium, which promise much success in a laboratory experiment made for the purpose of producing the effect I have described, as the greater number of substances which will bear a sufficient heat, are fragile, oxidable, or affected by water, yet general considerations from the nearest analogies in chemistry would lead us to expect a similar effect from all matter in a state of intense ignition; even assuming the presence of solid matter to be necessary, the catalytic effects of platinum are shared in different degrees by other substances: it therefore appears probable that at a certain degree of heat water does not exist as water or steam, but is resolved into its constituent elements. If, therefore, there be planets whose physical condition is consistent with an intense heat, the probability is, that their atmosphere and the substances which compose them are in a totally different chemical state from ours, and resolved into what we call elements, but which by intense heat may be again resolved into more subtle elements. The same may be the case in the interior of our planet, subject however to the counter agency of pressure.

The experiments strongly tend to support the views of Berthollet, that chemical and physical attraction are affinal, or produced by the same mode of force. All calorific expansions appear to consist in a mechanical severance of the molecules of matter; and if heat produce effects of decomposition merely by increase of intensity, there seems no reason why we should assign to it in this case a different mode of action from its normal one. On this view physical division carried on indefinitely must ultimately produce decomposition, and

chemical affinity is only another mode of molecular attraction. Thus a high degree of rarefaction, as at the bounds of the atmosphere, or in the interplanetary spaces, may entirely change the chemical condition of matter.

In a paper published in the Philosophical Transactions for 1843, p. 111, I have shown that we may oppose a chemical action by a physical one (electrolysis by a vacuum), that antagonizing chemical by physical tension, they mutually oppose each other. I believe the converse of this experiment has been made by M. Babinet, who by physical compression has prevented the development of chemical action.

I have also described in the Philosophical Magazine for November 1845, certain phænomena which appear to me to be irreconcileable with received chemical views; and though I then believed that the theory of Grotthus would be obliged to give way, I now incline to think that some of our chemical doctrines must ere long undergo a revision.

It is rather surprising that the valuable applications of which the phænomena of voltaic ignition are capable, and the fertile field which (as I believe) it presents for discoveries, both physical and chemical, should have been so completely neglected. It is true that until a recent period the imperfection of the voltaic battery rendered accurate and continued experiment on this subject difficult of performance, but still much might have been done. Davy made several experiments on the voltaic disruptive discharge, which in many points may be regarded simply as very intense ignition; but I am only aware of two experiments of his on voltaic ignition; one, in which he employed it in an exhausted receiver to examine to what extent the radiation of heat was carried on *in vacuo*; and another, already alluded to, in which, by immersing a portion of an ignited wire in water, he observed that it conducted in some inverse ratio to its heat.

I have made a vast number of experiments on the voltaic arc or disruptive discharge, in various media\*; when this is taken in a medium incapable of acting chemically on the electrodes, the phænomena are those of intense ignition of the terminals, which are dissipated in vapour and condensed upon the interior of the vessel in which the discharge is taken. I have examined some of these deposits, and they appear to consist of the metal of the terminals in a finely-divided state; this is strikingly shown with zinc. If the arc be taken between zinc points in an exhausted receiver, a fine dark powder, nearly black, is deposited on the interior, which, when collected, proves to be pure zinc, and on the application of a

\* Phil. Mag., June 1840; Literary Gazette and Athenæum, Feb. 7, 1845.

gentle heat, takes fire in the open air and burns into the white oxide: to casual observation the zinc would appear to be burned twice. The experiment appears to me to present an argument in favour of the dynamic theory of heat.

With charcoal, on the other hand, there is little or no deposit, but the charcoal continually yields carbonic oxide and hydrogen, and this for hours after the presence of water would be deemed impossible. I have taken the arc between pieces of well-burned charcoal for eight or nine successive hours, and there was still gas generated; indeed it appeared to be given off as long as there was any charcoal remaining, and a conversion of the carbon into inflammable gas might have been supposed. Much still remains to be done with this powerful agent, the voltaic arc: where, however, the object is simply to expose gases to an intense heat, the ignition of a conjunctive wire of platinum is more simple in its application, more uniform in its action, and instead of requiring a powerful battery, the effect can be satisfactorily produced by five or six cells, in many cases by two.

The heat is not so intense as that of the arc, but as it can be brought to within a few degrees of the fusing-point of platinum, it is far more intense than any heat usually employed in laboratories, certainly than any which can be applied to minute, I may say microscopic portions of gas or vapour.

In conclusion, I must express my sincere thanks to the managers of the London Institution, for having permitted me, as an honorary member, to carry on these experiments in the laboratory of the Institution.

London Institution, Aug. 21, 1846.

*XVIII. Supplementary Paper on certain Phænomena of Voltaic Ignition, and the Decomposition of Water into its constituent Gases by Heat. By W. R. GROVE, Esq.\**

**I**N selecting the above title, I endeavoured to give as clear an enunciation of the phænomena to be described in the paper as was consistent with the brevity usual in a title.

An exception has, however, been taken to it, that as the effects of decomposition are produced by ignited platinum, the phænomena may result from that obscure mode of action called catalysis. That I did not intend to exclude from consideration any possible action of the substance employed, will be evident from the paper itself, in which I have called attention to the general production of catalytic effects by solid bodies.

\* From the Philosophical Transactions for 1847, part i.; having been received by the Royal Society November 26, and read November 26, 1846.

Whatever value or novelty there may be in the facts I have communicated, is the same whether they be regarded as resulting from catalytic or from thermic actions. If the action be catalytic, it is one absolutely the reverse of that usually produced by platinum, and therefore just as much at variance with received experience as decomposition of water by heat would be; the effect of platinum, like that of heat, on the elements of water having been hitherto known only as combining them. With regard to any theoretic views I may have advanced, I by no means attach the same importance to them as I do to the facts themselves, though I consider it necessary for the collation of facts, and desirable for the progress of science, that an author pretending to communicate new results should give with them the impressions which led to their discovery, and the inferences which he regards as immediately deducible from them. No expression can be given to facts which does not involve some theory, and admitting the difficulty (perhaps insuperable) of correctly enunciating new phænomena, and the probability of future discoveries entirely changing our views regarding them, I cannot at present see that the title of my paper could be altered without being open to greater objections. I am of this opinion, not so much because other bodies than platinum will produce the effect, as I shall presently show, nor from the fact that the electrical spark will decompose aqueous vapour, though these are arguments in its favour; but from the following considerations. The catalytic action of platinum will induce or enable combination to take place where there is already a strong affinity or tendency to combine, as with mixed oxygen and hydrogen gases; it will also induce decomposition where the affinities are extremely weak, or in a state of unstable equilibrium, as in Thenard's peroxide of hydrogen; again, where there are nicely-balanced compound affinities, it may change the chemical arrangement of the constituents of a compound, but I do not know of any case in which a powerful chemical affinity can be overcome by catalytic action; to effect this we require some natural force of greater intensity than that to be overcome. We might as well say that the platinum electrodes of a voltaic battery decompose water, as to say that platinum decomposes it in the case in question; there, the force of electricity acts only by means of matter, and matter of a peculiar description; its action also is only perceptible at the surface of this matter. I seek to use the expression in my title with reference to heat in a similar sense to that in which we use similar terms with reference to electricity, *i. e.* to regard heat as the immediate dynamic force which overcomes the

affinity; thus, as we say when employing the voltaic battery, that we decompose water by electricity, so here we should say that we decompose it by heat.

If it be said that heat so weakens or antagonizes the affinity of the elements of water as to enable catalytic action to separate them, this amounts to the same theory, as heat is then regarded as the antagonizing force, and in this case the action, both thermic and catalytic, is the reverse of the normal action. I have thought it desirable shortly to discuss this question as likely to lead to further investigation, though I have been somewhat embarrassed by the want of definite meaning in the term catalysis; I must plead guilty to have frequently used the term, but notwithstanding, or perhaps on account of, its convenience, it has I fear had an injurious effect on scientific perspicuity.

The following experiments were made to ascertain whether platinum was the only substance by which the effect could be produced. A knob or button of the native alloy of iridium and osmium of the size of a small pea was formed by the voltaic battery; to this was attached by fusion another smaller knob of the same metal one-fourth the size of the former, and to this smaller one was attached a stout platinum wire; the object of the second knob was both to prevent the fusion of the platinum wire and also to avoid the possibility of any surface of platinum being exposed to the recipient tube or alloyed with the metal to be heated. The preparation of this simple instrument was very troublesome, but when made it answered the purpose well; the larger button could be fully ignited to an intense glow, while on account of the narrow neck which united them, the smaller was barely red-hot, and the platinum wire not perceptibly ignited. An experiment having been made with this metallic button and prepared water, similar to that previously made with platinum, gas was given off which averaged 0·3 of mixed gas; the residue was nitrogen mixed with varying small quantities of oxygen. The effect, upon the whole, was decidedly inferior to that of the platinum. Indeed as platinum is the most dense and unalterable of all known substances, it would be likely, upon any received theory of heat, to produce the greatest effects.

I tried palladium in the same manner; the gas yielded was hydrogen with small quantities of oxygen, and the water was stained with the oxide of the metal.

I now tried silica and other oxides, but the results were not very satisfactory. A spheroid of silica was formed by fusing pulverized silica on to a platinum wire, so as to cover it for the length of 0·4 of an inch; when this was plunged into

the hot water and again fused in the oxyhydrogen blowpipe, it constantly became frothed with small bubbles of vapour, and after a few experiments generally separated in fissures; in the experiment which was continued for the longest time without disintegration, the gas given off contained 0·15 of oxyhydrogen gas; from the whole result I believe there is an action of the water on the silica (probably forming a hydrate decomposable by heat) which is a bar to satisfactory results. With other oxides, at least such as would bear an intense heat, the difficulties were still more insuperable. Priestley has shown that water will corrode glass, and if I mistake not, others have shown the same effect produced on silica.

Although, as applied to the facts detailed, I attached no further meaning to the title of my paper than that which I have above stated, yet in one or two theoretical inferences I have certainly gone further; for instance, when I suppose the possibility or probability of mechanical rarefaction producing the same effects as heat, here (although I do not, indeed I cannot conceive the existence of heat without matter) I certainly abstract from the proposition any consideration of solid matter. In order to ascertain how far this view might be founded on truth, I had thought of making a few experiments on the effect of mechanical rarefaction on the tendency of gases to combine, but (in addition to the interference of necessary occupations) I find that M. de Grotthus has already experimented on the point; his experiments, as far as they go, corroborate the views I have put forth.

He finds\* that mixed gases, such as chlorine and hydrogen, or oxygen and hydrogen, when rarefied either by slow increments of heat or by the air-pump, do not take fire ("ne s'enflamme pas") by the electric spark. From the context, he evidently means that the gases will not detonate or unite in volumes, as he states that a partial combination ensues. Grotthus appears to have considered the combination of gases by the electric spark as an effect of sudden compression or molecular approximation, certain particles being brought within the range of their affinities by the sudden dilatation of others. Although he did not pursue the subject far enough to ascertain whether a degree of rarefaction could be reached which would be an actual bar to combination, still his experiments strengthen those views which assimilate mechanical and thermic molecular repulsion, and regard chemical affinity as being antagonized by physical repulsion.

Pursuing the series of analogies from the decomposition of euchlorine at a low temperature, that of ammonia at a higher,

\* *Annales de Chimie*, vol. lxxxii.

that of metallic oxides at a higher, and so on to oxide of hydrogen, there appears to be an extensive series of facts which afford strong hope of a generalized antagonism between thermic repulsion and chemical affinity, and a consequent establishment of the law of continuity in reference to physical and chemical attraction.

The deposit from chlorine, to which I have alluded in my paper, I have since examined, and though it differs in colour from that described in books, I find it is a protochloride of platinum, formed at the expense of the platinum wire. The larger portion of the chlorine in the tube combines with the hydrogen of the aqueous vapour, and the muriatic acid is absorbed by the water; when the experiment terminates the gaseous volume is reduced to nearly one-half, and this residue is oxygen.

This effect induced me to try an ignited wire on other analogues of chlorine, and I tried bromine and chloride of iodine in the apparatus (fig. 5). The tube was filled with the liquid, and its extremity was in the first experiments immersed in another narrow tube of the same liquid as that which filled it. When the platinum wire was ignited, permanent gas was given off both from the bromine and from the chloride of iodine, which gas on examination proved, to my surprise, to be oxygen. In one experiment I collected half a cubic inch of gas from an equal volume of chloride of iodine. As the experiment in this form required too large a quantity of the liquid to enable me to observe any change which might take place in its character, I repeated it with a tube five feet long, bent in two angular curves. A small quantity of the liquid was placed in the extremity of the tube containing the wire, which was so arranged as to be the lowest point; the angles were placed in cold water and the experiment proceeded with; my object was to enable the dense vapour of the liquids to shelter them from the atmosphere, there being no satisfactory method of shutting them in and yet allowing room for the elimination of the liberated gas, or of absorbing the latter by combination without also absorbing the vapours.

I had hoped by the above means to proceed with the experiments until all the oxygen was liberated that could be driven off, and then to have examined the residua; but I found that after experimenting for a short time, both the platinum wire and the glass in proximity to it were attacked by the liquids; this difficulty, similar to those which have hitherto prevented the isolation of fluorine, I have not yet been able to conquer, though I hope to resume the experiments.

As chloride of iodine is decomposed by water, it cannot

contain any notable quantity of the latter, but, until the experiments are carried further, it must remain a question whether the oxygen results from a small quantity of water contained in the liquid, the hydrogen combining with the liquid itself, or from a decomposition similar to that of the peroxides. The experiments certainly add a new and striking analogy to those already known to exist between the peroxides and the halogens, but they do not, as far as I have hitherto carried them, necessarily prove analogy of composition.

In conclusion, I would call attention to a point which I omitted to notice in my original paper, viz. the explanation afforded by the results contained in it of the hitherto mysterious phenomena of the non-polar decomposition of water by electrical discharges, as in the experiments of Pearson and Wollaston. This class of decompositions may now be carried much further. With the exception of fused metals, I know of no liquid, which, when exposed to intense heat such as that given by the electric spark, the voltaic arc, or incandescent platinum, does not give off permanent gas; phosphorus, sulphur, acids, hydrocarbons, water, salts, bromine and chloride of iodine, all yield gaseous matter.

Viewing these effects simply as facts, and without entering on any theoretical explanations or speculations, I cannot but think that there is a remarkable generality pertaining to them worthy of the most careful attention.

The apparatus I have described, particularly that represented by fig. 5, and the numerous applications of voltaic ignition which will occur to those who duly consider the subject, promise, I venture to believe, new methods and powers of investigating the molecular constitution of matter, and will, I trust, lead to many novel and important results.

Nov. 10, 1846.

**XIX. On the Modification of the Doubly Refracting and Physical Structure of Topaz, by Elastic Forces emanating from Minute Cavities. By Sir DAVID BREWSTER, K.H., D.C.L., F.R.S., and V.P.R.S. Edin.\***

[With a Plate.]

WHILE examining, in polarized light, the form and structure of the numerous crystals which I had discovered in the fluid cavities of topaz, my attention was particularly called to certain optical phenomena exhibited in other parts of the specimen. These phenomena, when first

\* Read before the Royal Society of Edinburgh on the 20th of January 1845, and published in their Transactions, vol. xvi. part 1. p. 7.

presented to me, were very indefinite in their character, and very imperfectly developed; but after a diligent examination of nearly 900 specimens of topaz, I succeeded in obtaining the most satisfactory exhibition of them under various forms, and in various degrees of intensity.

When an elastic force is propagated from a centre, in a soft and compressible medium, an increase of density is communicated to the surrounding mass,—of a temporary nature if the medium is a hard solid, like glass, but of a permanent nature if the medium is soft, and becomes indurated during the continuance of the compressing force. Both these effects may be exhibited experimentally; the first by a pressure upon glass, and the second by the action of an expanded bubble of air upon gum in a state advancing to induration.

The physical change thus produced in the transparent medium, whether it be temporary or permanent, may be exhibited to the eye in two ways; either by the property of the compressed parts in depolarizing light, or in the unequal refraction of common light produced by a varying density, and consequently a varying refractive power. In the *first* of these cases, the depolarizing action is displayed in the production of four quadrants of light, separated by the radii of a black rectangular cross, similar to the central portion, or the tints of the first order, in the uniaxal system of polarized rings; and, in the *second* case, the inequality of refractive density is shown by the mirage of a luminous point, in the form of concentric circles surrounding the centre of force, each circle marking successive actions of the central force.

When the four luminous quadrants of depolarized light, shown at A, B, C, D in Plate I. fig. 1, first presented themselves to me, I had some difficulty in perceiving the seat of the force, by which I believed that they were produced. The centres, or intersections of the black cross, were either too deep beneath the surface of the topaz, or too much covered by fluid cavities, to be seen; but by removing the part of the crystal which contained these cavities, I succeeded in finding that in every case there was a minute cavity in the centre of the luminous quadrants, or at the intersections of the arms of the black cross, from which the compressing force had emanated. One of these cavities is shown at E, fig. 2. It is of a quadrangular form, like the section of a rhomboidal prism, sometimes elongated, and sometimes of a slightly irregular shape. When perfectly regular, these cavities are between the 3000<sup>dth</sup> and the 4000<sup>dth</sup> of an inch in diameter. They are always dark, as if the elastic substance which they contained had collapsed into an opaque powder; and I have met

with only one case in which there seemed to be a speck of light in the centre. The degree of compression to which the topaz has been subjected is measured by the polarized tint developed in the luminous quadrants. It varies from the faintest pale *blue* to the *white* of the first order. In one case I found the luminous quadrant of one cavity coinciding with a luminous quadrant of another cavity, and thus producing the sum of their separate tints. This effect is shown in fig. 3.

In the phænomenon now described, the elastic force has spent itself in the compression of the topaz. The cavity itself has remained entire, without any fissure by which a gas or a fluid could escape. I have discovered, however, other cavities, and these generally of a larger size, in which the sides have been rent by the elastic force; and fissures, from *one* to *six* in number, propagated to a small distance around them. These fissures have modified the doubly refracting structure produced by compression; but, what is very interesting, no solid matter has been left on the faces of fracture, such as that which is invariably deposited, when an ordinary cavity, containing one or both of the two new fluids, is exploded by heat. The form of some of the cavities which have suffered this disruption is shown in fig. 4.

The influence of the compressing forces in altering the density, and consequently the refractive power of the topaz, is so distinctly seen in common light as to indicate the phæno-mena that are seen under polarized light. When the cavity is most distinctly perceived, it is surrounded with luminous and shaded circles, as shown in fig. 5; and traces of these are distinctly seen, as shown in fig. 6, when the specimen is examined in polarized light.

The cavities now described have obviously no resemblance whatever to those which I have described in previous papers as containing two new fluids. When any of the latter are either burst by heat, or exposed under high temperatures to the compressing forces of the fluids which they contain, they exhibit none of the phænomena peculiar to the former. The doubly refracting structure suffers no change; and when the cohesive forces of the crystal are overpowered, the faces of most eminent cleavage separate, and are covered with translucent crystalline particles, which the evaporated or discharged fluids leave behind.

The peculiar character of the *pressure cavities*, as we may call them, is still further evinced by the nature of the specimens in which they occur. I have never found them accompanying the ordinary cavities with two fluids. The specimens which contain them have imbedded in them numerous crystals,

differing little in their refractive power from topaz, and exhibiting in polarized light the most beautiful colours, varying with the thickness of the crystal, and diminishing in intensity as their axes approach to the plane of primitive polarization.

It is impossible to review the preceding facts without arriving at the conclusion, that the topaz must have been in a soft and plastic state when it yielded to the compressing force which emanated from the cavities; and that a mineral body thus acted upon could not have been formed, according to the received theory, by the aggregation of molecules having the primitive form of the crystal.

In a letter to Sir Joseph Banks, printed in the *Philosophical Transactions* for 1805, I deduced, from my experiments on depolarization, the existence of a new "species of crystallization, which is the effect of time alone, and which is produced by the slow action of corpuscular forces;" and I have remarked that "this kind of crystallization will probably be found to have had an extensive influence in those vast arrangements which must have attended the formation of our globe." These views have been confirmed by various new facts, wholly independent of each other;—by the existence of crystals imbedded in topaz, and having their axes in all possible directions, but especially by the nature and form of the strata of fluid cavities in that mineral. These strata cut at all inclinations the primary and secondary planes of the crystal. They are bent in the most capricious manner, forming planes of double curvature; and, what is also true of individual cavities stretching in every possible direction, they could never have been formed but when the topaz was in a soft and plastic state.

An objection to these views may be drawn from the fissures which proceed from the pressure cavities. The topaz must, doubtless, have been indurated when these fissures took place; but it is equally obvious that the depolarization produced by compression must have previously existed, and it is probable that the fissures were produced after the crystal had been removed from its matrix, and when, from cleavage or otherwise, its cohesive forces had been diminished.

St. Leonard's College, St. Andrews,  
January 16, 1845.

*XX. Researches on the Composition and Characters of certain Soils and Waters belonging to the Flax districts of Belgium, and on the Chemical Constitution of the Ashes of the Flax Plant. By Sir ROBERT KANE, M.D., M.R.I.A.*

[Continued from p. 45.]

*3. Results of the Examination of the Ashes of Flax grown upon the Soils previously analysed.*

A. This was coarse flax; and the flax of this district is usually of rather poor quality. It is however in most cases sown late, about the 15th of May.

On incineration, this flax was found to give of pure ash, in average, 4·237 per cent.

The stem, dried at 212°, and analysed, was found to contain 0·982 per cent. of nitrogen.

The ash contained, per cent., after deducting the sand and charcoal, which can be considered but as accidentally present:

Potash . . . . .	7·697
Soda . . . . .	19·186
Lime . . . . .	15·379
Magnesia . . . . .	3·446
Oxide of iron . . . . .	4·501
Alumina . . . . .	0·444
Oxide of manganese . . . . .	a trace
Sulphuric acid . . . . .	6·280
Phosphoric acid . . . . .	11·206
Carbonic acid . . . . .	20·599
Chloride of sodium . . . . .	8·213
Silica . . . . .	3·056
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	100·000

B. This flax was of the very best description, and was grown from first-class seed.

The stem, dried at 212°, and analysed, was found to contain per cent 0·756 of nitrogen.

On incineration, the plant, dried at 212°, yielded in average 5·434 per cent. of pure ash.

After deducting the sand and charcoal accidentally present, the ash was found to contain per cent., —

Potash . . . . .	22·897
Soda . . . . .	none
Lime . . . . .	16·483
Magnesia . . . . .	3·332
Peroxide of iron . . . . .	1·523
Alumina . . . . .	0·438
Oxide of manganese . . . . .	a trace
Sulphuric acid . . . . .	6·174
Phosphoric acid . . . . .	11·802
Carbonic acid . . . . .	25·235
Chloride of sodium . . . . .	8·701
Silica . . . . .	3·409
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	99·994

C. This flax was very fine, and was said to be as good as any grown in that season.

The stem, dried at 212°, and analysed, was found to contain, per cent., 0·876 of nitrogen.

On incineration, the plant, dried at 212°, yielded in average 3·670 per cent. of pure ash.

After deducting, as usual, the sand and charcoal, the ash was found to contain per cent.,—

Potash . . . . .	22·303
Soda . . . . .	14·116
Lime . . . . .	18·525
Magnesia . . . . .	3·933
Peroxide of iron . . . . .	1·100
Alumina . . . . .	0·725
Oxide of manganese . . . . .	a trace
Sulphuric acid . . . . .	6·833
Phosphoric acid . . . . .	8·811
Carbonic acid . . . . .	16·383
Chloride of sodium . . . . .	4·585
Silica . . . . .	2·678
	<hr/>
	99·992

D. This flax, of a rather coarse quality, had been sown May 2nd, and pulled July 29.

The plant, dried at 212° and analysed, yielded 0·901 per cent. of nitrogen.

On incineration after desiccation, it gave 4·543 per cent. of ashes.

The composition of the ash per cent. was—

Potash . . . . .	25·790
Soda . . . . .	·429
Lime . . . . .	19·098
Magnesia . . . . .	3·648
Peroxide of iron . . . . .	2·281
Alumina . . . . .	none
Oxide of manganese . . . . .	none
Sulphuric acid . . . . .	12·091
Phosphoric acid. . . . .	10·983
Carbonic acid . . . . .	9·895
Chloride of sodium . . . . .	12·751
Silica . . . . .	<u>3·030</u>
	99·996
Loss . . . . .	<u>·004</u>
	100·000

H. The flax grown upon the Dutch soil yielded, on analysis, 1·000 per cent. of nitrogen, when dried at 212° Fahrenheit.

It also gave, by incineration, 5·151 per cent. of ashes, of which the composition per cent. was found to be as follows:—

Potash . . . . .	18·410
Soda . . . . .	10·912
Lime . . . . .	18·374
Magnesia . . . . .	3·023
Peroxide of iron . . . . .	2·360
Alumina . . . . .	1·439
Oxide of manganese . . . . .	none
Sulphuric acid . . . . .	9·676
Phosphoric acid . . . . .	11·058
Carbonic acid . . . . .	13·750
Chloride of sodium . . . . .	5·655
Silica . . . . .	<u>5·327</u>
	99·984
Loss . . . . .	<u>·016</u>
	100·000

If we examine somewhat in detail the results of the ash analyses above given, there will be found several points worthy of attention, in reference to the probable laws of replacement of acids and bases, as mineral constituents of plants; and also with regard to the necessary presence of certain materials.

It will be seen that in all cases a large proportion of the bases of the ash had been combined with organic acids, and were hence found in the ash as carbonates. This quantity is,

however, variable; and it will be seen that a variation takes place in the quantity of sulphuric acid exactly of an opposite character; so that in the plant, the proportions of organic salts and of sulphates would appear to have been such, that an increase in one replaced any deficiency of the other. Thus when the quantity of carbonic acid in the ash was 25·235, the sulphuric acid was 6·174; but when the sulphuric acid was 12·091, the carbonic acid fell to 9·895. I do not however mean absolutely to assert that the sulphuric and the organic acids of the plant are, in all cases, or exactly, mutually replacing.

The small quantity, as well as the narrow limits of fluctuation of the silica, is worthy of notice; particularly when compared with that which I shall have to notice as regards the composition of Irish flax. It does not appear connected with any of the bases in particular, nor to follow any special variation among them.

There is nothing more peculiarly characteristic in the composition of the ashes of the flax plant, than the quantity of phosphoric acid which is found therein. In order to bring this into full evidence, I shall extract from the works of other chemists the determination of the quantity of phosphoric acid in the ash yielded by the stems of other plants.

Tobacco stalk and leaves . . . . .	2·73
Wheat stems . . . . .	3·10
Oat stems . . . . .	3·00
Clover plants . . . . .	6·30

The stems of flax are, then, more than double as rich in phosphoric acid as the stems of even the cereal grasses or leguminous plants; and if we even look to the constitution of the ash of many substances used as food by man, we shall find that, in 100 parts, there are from the ash of—

Oats . . . . .	14·9	phosphoric acid
Potatoes . . . . .	11·3	...
Turnips . . . . .	6·1	...

whilst the average of the analyses of Belgian and Dutch flax ashes show that there are present no less than 10·77 per cent. It was this enormous quantity of the most valuable ingredient of manure that first impressed me with the importance of its œconomy, and induced me to endeavour to fix the attention of agriculturists upon the fact; for if we calculate, from the produce per acre, the quantity of phosphoric acid taken from a statute acre of ground by an ordinary crop of any of the usual kinds, we shall find that it amounts in the case of flax to very nearly as much as with any of the ordinary grain or root crops;

and that whilst the mineral elements of these are what the value really consists in, the value of the flax is altogether independent of those constituents, which are thus so much real loss to the farmer.

Hence, under the ordinary plan of cultivation, farmers were certainly in the right to consider it one of the most exhausting crops; and that its place in rotation should be equivalent to that of a grain crop, which it ought by no means to follow, or be followed by; whereas, under a system of management which should allow of the proper œconomy of its mineral constituents, that are separated in the processes of watering and dressing, the phosphoric acid and other materials might be restored to the manure heap or to the field, and the crop of flax be thus deprived of those permanently exhausting qualities which it now possesses.

It will be interesting further to notice the constitution of these ashes, under a point of view which has been put forward by some chemists, as possessing the character of a general rule or law; to wit, that although the individual bases present in an ash may vary very much, and even some (as in one of the ashes analysed, B soda) may be totally absent, yet the sum of the oxygen present in the bases will be found to be constant. If we apply that rule to the ashes above analysed, we shall find—

Title of ash.	Quantity of oxygen in bases.
A . . . . .	13·73
B . . . . .	10·95
C . . . . .	14·65
D . . . . .	13·45
H . . . . .	13·60
Average .	13·28

There is certainly a close agreement among these numbers; and if we excluded one analysis (B), which is also exceptional in containing no soda, it should decidedly appear that the quantity of oxygen present in the bases of 100 parts of ash was represented by a constant number (13·86). It will be found that the analyses of Irish flax lend support to this view; but I think that we shall require very many more analyses before we can fix upon it as a positive law.

In order to afford comparison with the results above given, I have extended my analyses of Irish flax; and as there appear one or two remarkable points of difference between them, I shall notice also my prior results.

The flax I originally experimented on was grown at my own residence, a short distance from Dublin. It yielded,

when dried at  $212^{\circ}$ , 0·56 of nitrogen per cent., and 5 per cent. of ashes, consisting of, in 100 parts,—

Potash . . . . .	9·78
Soda . . . . .	9·82
Lime . . . . .	12·33
Magnesia . . . . .	7·79
Alumina . . . . .	6·08
Phosphoric acid . . . . .	10·84
Sulphuric acid . . . . .	2·65
Carbonic acid . . . . .	16·95
Chlorine . . . . .	2·41
Silica . . . . .	21·35
	100·00

I selected for another analysis a specimen of flax given to me by William Blacker, Esq., which had received a prize at the Market-hill show by the tenants of the Earl of Gosford. When dried at  $212^{\circ}$ , this flax yielded 0·672 per cent. of nitrogen, and 5·572 per cent. of ashes, which contained per cent.—

Potash . . . . .	6·332
Soda . . . . .	6·350
Lime . . . . .	22·699
Magnesia . . . . .	4·058
Peroxide of iron . . . . .	13·520
Oxide of manganese . . . . .	1·092
Alumina . . . . .	none
Sulphuric acid . . . . .	8·929
Phosphoric acid . . . . .	7·002
Carbonic acid . . . . .	4·107
Chloride of sodium . . . . .	0·901
Silica . . . . .	24·978
	99·968

There is first to be remarked the very curious circumstances of both Irish specimens containing a large quantity of silica, from 21 to 25 per cent., whilst the Belgian and Dutch flax contained only from 3 to 5 per cent. In the Dublin flax there is no particular replacement to which this could be attributed; but in the Armagh flax, the small quantity of carbonic acid, only 4 per cent., shows that the organic acids had been but little generated in the plant, and probably a quantity of silica was substituted for them. The question of whether this large quantity of silica, which, however, is mostly removed from the fibre along with the other materials during its dressing, could produce in it any degree of hardness or brittleness, is very well worthy of the attention of the philosophical agriculturist.

It is remarkable also, that in both Irish flaxes the potash and soda are present in equal quantities, though not in the same quantity in each ash. This, however, may be only a coincidence, though still a remarkable one.

A more interesting peculiarity is the presence, in the Armagh flax, of the very large quantity of peroxide of iron, 13·5 per cent. In the Dublin flax I have not formerly counted iron as an ingredient, although I did find in the analyses a small quantity, because I had burned the plants on a sheet of iron wire-gauze, and I feared that a minute quantity of iron might be derived from that; and also that, in that analysis, my only object was to show the presence of large quantities of valuable ingredients, which the farmer ought to economise. I therefore did not separately determine that minute trace of iron, which, however, could in no way affect the numerical results. The occurrence of the large quantity of iron in the Armagh flax is, therefore, the more curious; and it will be interesting to examine, by other analyses of the flax sown in the sand-stone districts of the north of Ireland, whether the same proportion of oxide of iron will be found.

Notwithstanding the great difference in the quantity of silica in the Irish flaxes from the Belgian, the proportion of oxygen per cent. in the bases comes out nearly the same. Thus the bases contain of oxygen,—

Flax from Dublin . . . . .	13·41
Flax from Armagh . . . . .	13·66

closely coinciding with the number already found for the Belgian and Dutch flax.

It is not unimportant to correct a statement recently made, that prepared fibre of flax is not so destitute of mineral constituents as I have assumed in the preceding investigations. In order to arrive fully at the truth, I have instituted some additional experiments, with the following results:—

A. Very imperfectly dressed flax from the county Clare gave, by incineration, with proper precautions, 0·97 per cent. of ashes, containing principally oxide of iron and lime.

B. A specimen of perfectly dressed flax from Belfast gave, on incineration, 0·62 per cent. of ashes.

C. A specimen of fine dressed linen gave, on incineration, 0·24 per cent. of ashes, principally lime, with some oxide of iron. Hence it is evident that my former results on this point were precisely confirmed by these new trials.

#### 4. *Results of the Examination of the Waters selected for steeping Flax in Belgium.*

No. 1. This water is from a large pond near the bank of

the Scheldt, which has been most likely formed by digging out peat for fuel, as the soil near it is peat, and as in neighbouring ponds peat is now scraped up from the bottom, and prepared for fuel by drying in the sun. This water is renewed by the overflowing of the Scheldt, and is apparently not at all peaty.

This water was pretty clear, but contained some suspended matter. When 100,000 grains were evaporated to dryness there was obtained 51.70 grains of residue, consisting of, in 100 parts,—

Protoxide of iron . . . . .	·514
Lime . . . . .	6.940
Magnesia . . . . .	·856
Soda . . . . .	28.620
Potash . . . . .	8.740
Sulphuric acid . . . . .	8.054
Muriatic acid . . . . .	25.765
Phosphoric acid . . . . .	no trace
Carbonic acid, with organic matter and loss . . . . .	20.511
	100.000

No. 2. Water from one of the best Bloe retting pits, near Hamme Log, in Belgium. This water is also supplied from the Scheldt annually, before the retting season commences, and left to stand in the pit for six or eight weeks. The top becomes covered with green weeds which are cleared off immediately the flax is put in. This causes the water to be muddy, as there is a considerable thickness of mud at the bottom which is disturbed, the workmen standing in the pit when cleaning the top of the water. The flax is then laid in; and after laying two or three layers, they shovel up some of the mud in the bottom to put on the flax to sink it; and when the pit is full, the flax is covered by about an inch thickness of mud. This sample was taken from a pit which had just been disturbed and muddled by cleansing the top of weeds, preparatory to putting the flax in.

This water was found very muddy, but the suspended matter was principally organic.

100,000 grains left by evaporation 139.69 grains of solid matter, of ochrey appearance, and consisting, per cent., of—

Protoxide of iron . . . . .	6·633
Lime . . . . .	8·435
Magnesia . . . . .	1·369
Soda . . . . .	11·607
Potash . . . . .	4·181
Sulphuric acid . . . . .	8·435
Muriatic acid . . . . .	8·682
Phosphoric acid . . . . .	no trace
Carbonic acid, with organic matter and loss . . . . .	50·658
	100·000

No. 3. This water is from a large pond similar to that from which No. 1 is taken, but from a different part of the country, and a much larger body of water.

It was clear, containing but very little suspended matter.

100,000 grains left on evaporation 50·68 grains of solid residue, which consisted of, per cent,—

Protoxide of iron . . . . .	2·584
Lime . . . . .	17·829
Magnesia . . . . .	1·530
Soda . . . . .	30·232
Potash . . . . .	15·762
Sulphuric acid . . . . .	11·627
Muriatic acid . . . . .	2·580
Phosphoric acid . . . . .	no trace
Carbonic acid, with organic matter and loss . . . . .	17·856
	100·000

No. 4. This water is from the river Lys, so celebrated for its steeping qualities. It was taken from the river in France before it had reached the highest retting place. The specimen was clean, but there was some suspended matter, principally organic.

100,000 grains, evaporated to dryness, left a residue of 45·11 grains, consisting of, in 100 parts,—

Protoxide of iron . . . . .	6·200
Lime . . . . .	5·484
Magnesia . . . . .	1·192
Soda . . . . .	28·298
Potash . . . . .	5·405
Sulphuric acid . . . . .	9·300
Muriatic acid . . . . .	7·754
Phosphoric acid . . . . .	·079
Carbonic acid, with organic matter and loss . . . . .	36·288
	100·000

No. 5. This water was from a retting pit in Holland.  
100,000 grains, evaporated to dryness, gave a residue of  
42·4 grains, which consisted, per cent., of—

Protoxide of iron . . . . .	1·183
Lime . . . . .	3·613
Magnesia . . . . .	7·601
Soda . . . . .	19·277
Potash . . . . .	8·205
Sulphuric acid . . . . .	5·607
Muriatic acid . . . . .	9·439
Carbonic acid, with organic matter and loss. . . . .	45·075
	100·000

With regard to the constitution of these several specimens of water, it can only now be remarked, that in all there was present a large quantity of mineral impurities; and that in Nos. 2 and 4, the very samples which are of the most remarkable and celebrated steeping waters in Belgium, a large quantity of iron is present, so that they might be in a degree termed chalybeate waters. How this regards their excellence for preparing flax I do not pretend to say, and indeed it will require much more extended investigation before a satisfactory solution of it can be given.

All these waters are further remarkable for containing a larger quantity of potash than ordinary waters are found usually to have. I shall not, however, enter minutely into the discussion of their constitution, as I shall have to resume the subject at another time; and I wish only to place on record for the present the analytical results which the samples of waters forwarded to me from Belgium by Mr. Marshall, had afforded.

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## XXI. On the Theoretical Velocity of Sound. By J. P. JOULE\*.

THE celebrated French mathematician De Laplace has, it is well known, pointed out that the heat evolved by the compression of air is the cause of the velocity of sound, according to the theory of Newton, being so much less than that actually observed. He has also given a formula by which the velocity may be determined when the ratio of the specific heat of air at constant pressure to that at constant volume is known. The determination of the elevation of temperature in air by compression has however been hitherto attended with difficulty, and hence the theorem of De Laplace has never yet been fairly compared with experiment. I was therefore anxious

\* Communicated by the Author.

to ascertain how far the mechanical equivalent of heat, as determined by my recent experiments on the friction of fluids, might be able to contribute to clear up this question.

The capacity of air at constant pressure, according to the experiments of De la Roche and Berard, is  $0\cdot2669$ . Consequently a quantity of heat capable of increasing the temperature of a lb. of water by  $1^{\circ}$ , will give  $1^{\circ}$  also to  $3\cdot747$  lbs. of air, while the air will be expanded  $\frac{1}{491}$ ; an expansion in which a force equal to  $200\cdot7$  lbs. through a foot is expended in raising the atmosphere of the earth. The equivalent of a degree of heat per lb. of water, determined by the careful experiments brought before the British Association at Oxford, is  $775$  lbs. through a foot. Hence  $200\cdot7$  lbs. through a foot is equal to  $0\cdot259$ .

We see, therefore, that for every degree of heat employed by De la Roche and Berard in expanding and heating air,  $0\cdot259$  was occupied in producing the mechanical effect, leaving  $0\cdot741$  as that actually employed in raising the temperature of the air. Hence the actual specific heat (commonly called capacity at constant volume) is  $0\cdot2669 \times 0\cdot741 = 0\cdot1977$ . Taking this as the specific heat of air and the equivalent  $775$ , it follows that if a volume of air of  $171\cdot6$  cubic inches be compressed to  $170\cdot6$  cubic inches, it will be heated  $1^{\circ}$ , a quantity of heat which will occasion an increased pressure of  $\frac{1}{491}$ . So that the celerity of sound will be increased by this means in the subduplicate ratio of  $491$  to  $661\cdot6$ , or in the simple ratio of  $2216$  to  $2572$ , which will bring it up from Newton's estimate of  $943$  to  $1095$  feet per ", which is as near  $1130$ , the actual velocity at  $32^{\circ}$ , as could be expected from the nature of the experiments on the specific heat of air, and fully confirms the theory of Laplace.

Oak Field, near Manchester,  
July 17, 1847.

## XXII. *On the Composition of Caffein, and of some of its Compounds.* By EDWARD CHAMBERS NICHOLSON, Esq.\*

**C**AFFEIN was first analysed by Professors Liebig and Pfaff † in 1832. The result of this investigation was confirmed by a subsequent analysis of Prof. Wöhler ‡.

In 1838 Professor Liebig induced M. Jobst § to analyse thein, who proved this body to be identical with caffein. His analyses gave the same results as his predecessors. The same remark applies to the experiments of Mulder || on thein,

\* Communicated by the Chemical Society; having been read Feb. 15, 1847.

† Liebig's *Annalen*, i. 17.      ‡ Ibid.      § Ibid. xxv. 63.

|| *Bulletin des Sciences Phys. et Nat. de Neerlande*. 1838, p. 32.

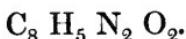
and also to an analysis which M. Martius \* made of guaranin, a substance, the identity of which with caffein and thein had previously been pointed out by Berthemot and Dechastelus†. Lately Dr. Stenhouse ‡, when examining Paraguay tea, has also made some analyses of thein.

The following table, in which I have recalculated these analyses according to the atomic weights, carbon 6 and hydrogen 1, allows a comparison to be made of the results obtained by these chemists.

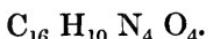
*Mean of the Analyses.*

	Caffein.		Thein.		Guaranin.	
	Liebig & Pfaff.	Wöhler.	Mulder.	Jobst.	Stenhouse.	Martius.
Carbon .	49·30	49·25	49·18	49·47	48·95	49·23
Hydrogen .	5·22	5·43	5·49	5·20	5·15	5·08
Nitrogen .	28·86		28·53	28·90		28·83

The most simple expression which can be deduced from these numbers is



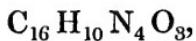
Stenhouse's analysis however of the platinum compound proves that this formula must be doubled, and that the atom of caffein or thein is



The theoretical numbers of this formula are the following:—

16 eqs. Carbon . . .	96	49·48
10 ... Hydrogen . . .	10	5·15
4 ... Nitrogen . . .	56	28·86
4 ... Oxygen . . .	32	16·51
	194	100·00

From these numerous experiments the composition of caffein might have been considered as perfectly established. In a recent investigation of coffee, however, M. Payen§ states that he has obtained results which differ very sensibly from those obtained by his predecessors, and which he has translated into the formula



which contains 1 equiv. of oxygen less than the formula up to the present time admitted.

The theoretical numbers of Payen's formula are—

16 eqs. Carbon . . .	96	51·43
10 ... Hydrogen . . .	10	5·35
4 ... Nitrogen . . .	56	30·34
3 ... Oxygen . . .	24	12·88
	186	100·00

\* Liebig's *Annalen*, xxxvi. 93.

† Ibid. xxxvi. 90.

‡ Mem. Chem. Soc., vol. i. pp. 215, 237. [Phil. Mag., xxiii. p. 426.]

§ Comptes Rendus de l'Académie, tome xxiii. 8.

We observe here a difference of 2 per cent. of carbon, which M. Payen has obtained over the results of the above-mentioned chemists.

In order to elucidate this discrepancy, Dr. Hofmann induced me to make some experiments under his direction, partly with a quantity of beautiful caffein which he gave me\* and partly with a specimen which I have prepared myself.

### *Caffein.*

To ensure perfect purity of the substance it was crystallized three times from dilute alcohol, washed and dried. Thus purified, it formed very beautiful long white prisms, perfectly transparent when dried in the air, but which became opake if exposed to a higher temperature. The crystals dried in the water-bath lost no weight when kept in an air-bath for four hours at a temperature of 130° C.

The specimen which I had prepared myself was obtained from Costa Rico coffee, by boiling the bruised fruit in water, precipitating the decoctions by basic acetate of lead and treating the filtrate with hydrosulphuric acid; after the whole of the lead had been removed, I evaporated the liquid to dryness in a water-bath, in order to get rid of acetic acid, and dissolved the residue in a small quantity of boiling water: upon cooling, the caffein crystallized out of a dark colour, and very impure. To purify it, it was washed and recrystallized three times from water, and finally from alcohol. It was then perfectly white, and had exactly the same appearance as the specimen which I obtained from Dr. Hofmann.

### *Analysis.*

I. 0·3827 grm. of substance, dried at 100° C. and burnt with chromate of lead, gave 0·6948 grm. of carbonic acid, and 0·1800 grm. of water.

II. 0·417 grm. of substance, burnt with chromate of lead and chlorate of potash, gave 0·7552 grm. of carbonic acid, and 0·1965 grm. of water.

III. 0·3934 grm. of substance of my own preparation gave 0·7123 grm. of carbonic acid and 0·1878 grm. of water, which calculated in 100 parts gives—

	I.	II.	III.
Carbon . . .	49·51	49·39	49·37
Hydrogen . . .	5·22	5·23	5·30

\* I owe this specimen, of great beauty, to the well-known kindness of Mr. E. Merck of Darmstadt.—A. W. H.

which agrees with Professor Liebig's formula, as is seen by the following:—

	Theory.	Mean of experiments.
16 cqs. Carbon . . .	96	49·48
10 ... Hydrogen . . .	10	5·15
4 ... Nitrogen . . .	56	28·86
4 ... Oxygen . . .	32	16·51
	<hr/> 194	<hr/> 100·00

### Caffein and Bichloride of Platinum.

On precipitating a solution of caffein in hydrochloric acid with bichloride of platinum, as Dr. Stenhouse has shown, a precipitate of an orange-yellow colour is obtained. If the two solutions are mixed hot, the fluid on cooling deposits the compound in beautiful granular crystalline tufts, which, when thrown on a filter and washed with alcohol, are perfectly pure. This double salt is only sparingly soluble in alcohol, æther, and water. It does not alter when exposed to light, nor does it lose in weight when kept at 100° C. for a considerable time.

The analyses of salts, all prepared at different periods and dried at 100° C., gave the following results:—

I. 0·5382 grm. of substance, burnt with chromate of lead, gave 0·4765 grm. of carbonic acid, and 0·1387 grm. of water.

II. 0·4881 grm. of substance gave 0·1196 grm. of platinum.

III. 0·4779 grm. of substance gave 0·1172 grm. of platinum.

IV. 0·6022 grm. of substance gave 0·1482 grm. of platinum.

V. 0·5781 grm. of substance gave 0·1425 grm. of platinum.

VI. 0·5246 grm. of substance gave 0·1293 grm. of platinum.

VII. 0·3847 grm. of substance made of caffein of my own preparation, gave 0·0945 grm. of platinum.

Which give the following per-centages:—

	I.	II.	III.	IV.	V.	VI.	VII.
Carbon . . .	23·80						
Hydrogen . . .	2·86						
Platinum ...	24·51	24·52	24·60	24·64	24·64	24·56	

leading exactly to the formula given by Dr. Stenhouse, viz.



as is seen when placed in comparison with the calculated numbers.

	Theory.	Mean of my experiments.	Dr. Stenhouse's mean.
16 eqs. Carbon . .	96·0	23·97	23·80
11 ... Hydrogen . .	11·0	2·74	2·86
4 ... Nitrogen . .	56·0	13·98	
4 ... Oxygen . .	32·0	8·02	
3 ... Chlorine . .	106·5	26·59	
1 ... Platinum . .	98·9	<u>24·70</u>	24·58
1 ... Caffein and bichloride of platinum	400·4	100·00	24·49

The analysis of caffein, as well as that of the platinum compounds, agree so perfectly with the numbers of Professor Liebig's formula, that there can be no doubt about its accuracy.

Assuming 1 equiv. of oxygen less in the equivalent of caffein, as is proposed by M. Payen, the platinum compound should contain not less than 24·46 per cent. of carbon and 25·12 of platinum. Now three determinations by Dr. Stenhouse, and six which I have made, never gave more than 24·64 per cent., that is, 0·6 per cent. less of platinum.

Not satisfied, however, with these proofs, I have tried to find some other compounds by which the atomic weight of caffein could be determined with equal accuracy.

In what follows a description of several new double salts of caffein will be given, the analyses of which correspond equally well with the original formula of this substance.

### *Caffein and Nitrate of Silver.*

This compound is obtained when a solution of nitrate of silver is added in excess to an aqueous or alcoholic solution of caffein. If the solutions are concentrated it falls down in white hemispherical nodules, which adhere firmly to the side of the vessel.

When washed with water and crystallized from alcohol it is absolutely pure. This compound is indistinctly crystalline, of a perfectly white colour, and if dry undergoes no change when exposed to light, but if moist acquires a purplish hue. It is very soluble in hot water and alcohol, sparingly soluble in cold, and may be boiled in either solvent without undergoing decomposition. It loses no weight in the water-bath, but at a higher temperature it is decomposed, caffein sublimes, and metallic silver is left.

*Analysis.*—When burnt with chromate of lead—

I. 0·4514 grm. of substance gave 0·4345 grm. of carbonic acid, and 0·1162 grm. of water.

II. 0·2500 grm. of substance gave 0·744 grm. of silver.

III. 0·2716 grm. of substance gave 0·810 grm. of silver, which give the following per-centages :—

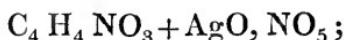
	I.	II.	II.
Carbon . . .	26·45		
Hydrogen . . .	2·86		
Silver . . . . .		29·76	29·82,

and the formula— $C_{16}H_{10}N_4O_4 + AgO, NO_5$ , as may be seen by the following calculation :—

	Theory.	Found.
16 eqs. Carbon . . .	96	26·37
10 ... Hydrogen . . .	10	2·74
5 ... Nitrogen . . .	70	19·23
10 ... Oxygen . . .	80	22·00
1 ... Silver . . . . .	108	29·66
	364	100·00

The only analogues to this singular compound which I know are those of urea and nitrate of silver, analysed by Werther\*: the formulæ of which are— $C_2H_4N_2O_2 + AgO, NO_5$ , and  $C_2H_4N_2O_2 + 2(AgO, NO_5)$ .

These compounds, however, in consequence of the peculiar nature of urea, are not very stable, being decomposed when boiled with water into nitrate of ammonia and cyanate of silver. There likewise exists a compound of nitrate of silver and glycocoll, lately described by Horsford†, having the formula



and, according to H. Rose, a compound of nitrate of silver with ammonia, 3 equivs. of this gas being absorbed by 1 equiv. of the former salt.

#### *Chloride of Mercury and Caffein.*

This beautiful compound is obtained when an aqueous or alcoholic solution of caffeine is added to a solution of chloride of mercury; the latter being kept in excess, the fluid remains perfectly clear, but after the lapse of a few seconds solidifies into a mass of very small crystals, which when recrystallized from water or alcohol and washed on a filter, are quite pure.

When pure and crystallized from water it is very similar in appearance to caffeine, the crystals not being however quite so large. It is very soluble in alcohol and water, hydrochloric, nitric, and oxalic acids, and seems to form with the latter a crystalline compound. It is nearly insoluble in æther. In reference to its constitution, it is distinguished from the dou-

\* Liebig's *Annalen*, lvi. 262.

† Ibid. ix. 36.

ble salt of platinum, for in this instance the caffein is in direct combination with the chloride of mercury, and is exactly analogous to the corresponding compounds of leucoline and aniline investigated by Dr. Hofmann\*. The mercurial compounds of this kind are generally easily decomposed, but the compound of chloride of mercury and caffein is so stable, that it may be boiled in water for a considerable time without undergoing the slightest change in its properties. It may be dried at 100° C. and loses no weight at that temperature.

I endeavoured to combine the determination of the carbon, hydrogen and mercury of this substance in *one* combustion, and have perfectly succeeded. The operation was conducted as follows:—The substance was mixed with chromate of lead and introduced into a combustion-tube of at least 26 inches in length. About 6 inches of copper turnings are placed above the mixture, leaving a space of 8 inches from the copper to the anterior end of the tube. A receptacle for the mercury is formed out of the tube itself by contracting it about an inch from the copper turnings, and again so as to leave an elongated bulb of an inch in length. At the close of the operation the tube is cut with a file at the posterior contraction. In order to separate the water from the mercury, the chloride of calcium tube (which has not been detached) is connected with an aspirator and air admitted through chloride of calcium, the bulb being kept at a temperature of 100° C.

I obtained in my analysis the following numbers:—0·7833 grm. of substance gave 0·5832 grm. of carbonic acid, 0·1639 grm. of water, and 0·3365 grm. of mercury, corresponding to the following per-cent-age, which I place in comparison with the theoretical numbers:—

	Theory.	Expt.
16 eqs. Carbon . . . . .	96	20·68 20·30
10 ... Hydrogen . . . . .	10	2·15 2·32
4 ... Nitrogen . . . . .	56	12·11
4 ... Oxygen . . . . .	32	6·89
2 ... Chlorine . . . . .	70	15·08
2 ... Mercury . . . . .	200	43·09 42·91
	464	100·00

### Caffein and Terchloride of Gold.

This compound is formed when a solution of terchloride of gold is added in excess to caffein dissolved in dilute hydrochloric acid. If concentrated solutions are employed, the whole immediately solidifies into a mass of a most splendid lemon-yellow colour; this is to be washed with cold water

\* Liebig's *Annalen*, xlvi. 37.

and crystallized from alcohol, and finally dried in the water-bath.

The crystals from an alcoholic solution are in the form of long needles, of an orange-yellow colour and a very bitter metallic taste; they are soluble in alcohol and water. When boiled in water for a short time, the salt is decomposed, a yellow flocculent matter precipitating, which is insoluble in alcohol, ether and water, but soluble in hydrochloric acid. If an aqueous solution is kept on the sand-bath for some hours at a temperature of about 68° C. it is also decomposed, and metallic gold separates in shining scales.

It is not altered when exposed to light, and when dry may be heated to 100° C. without undergoing decomposition.

*Analysis.*—When burnt with chromate of lead—

I. 0·8530 grm. of substance gave 0·5525 grm. of carbonic acid and 0·1622 grm. of water.

II. 0·3224 grm. of substance gave 0·1197 grm. of metallic gold.

III. 0·3019 grm. of substance gave 0·1115 grm. of metallic gold, which give the following per-centages:—

	I.	II.	III.
Carbon . . .	17·72		
Hydrogen . . .	2·11		
Gold . . .		37·12	36·93

corresponding to the formula  $C_{16}H_{10}N_4O_4HClAuCl_3$ , as may be seen by the following table, where the calculated and quantities found are placed in comparison:—

		Theory.	Found.
16 eqs. Carbon . . .	96·00	17·98	17·72
11 ... Hydrogen . . .	11·00	2·06	2·11
4 ... Nitrogen . . .	56·00	10·50	
4 ... Oxygen . . .	32·00	6·01	
4 ... Chlorine . . .	142·00	26·60	
1 ... Gold . . .	196·66	36·85	37·02
	533·66	100·00	

The caffein compounds which I have analysed are therefore—

Caffein . . . . .	$C_{16}H_{10}N_4O_4$ .
Platinum compound . . . . .	$C_{16}H_{10}N_4O_4HClPtCl_2$ .
Silver compound . . . . .	$C_{16}H_{10}N_4O_4AgO, NO_5$ .
Mercury compound . . . . .	$C_{16}H_{10}N_4O_42(HgCl)$ .
Gold compound . . . . .	$C_{16}H_{10}N_4O_4HClAuCl_3$ .

There exist several other double compounds of caffein, which I have however not subjected to analysis.

On mixing a hot alcoholic solution of caffein with an alcoholic solution of cyanide of mercury, beautiful needles of a double salt are deposited upon cooling, which correspond most likely to the mercury salt I have just described. A solution of caffein in hydrochloric acid gives a beautiful brown precipitate with chloride of palladium; and the filtered solution deposits another compound in the form of yellow scales, very similar in appearance to iodide of lead.

Caffein gives no precipitate with solutions of sulphate of copper, chloride of tin, acetate of lead, and nitrate of suboxide of mercury. When boiled with sesquichloride of iron, a reddish-brown precipitate subsides upon cooling, which is perfectly soluble in water, and is most likely a double compound of caffein and sesquichloride of iron.

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XXIII. Note in reference to the extension of Euler's Theorem.

By J. R. YOUNG, Professor of Mathematics in Belfast College.

To Richard Taylor, Esq.

DEAR SIR,

IN the Philosophical Magazine for June last a communication of mine was published respecting an extension of a certain theorem of Euler concerning the products of the sums of squares. At the time that notice was written, I was under the impression that the theorem admitted of an extent of generalization which a further investigation of the matter proves to me has not place. I am now prepared to show that the proposition does not hold beyond the case for eight squares, the formulæ for which I have already printed in the Proceedings of the Royal Irish Academy; in the Transactions of which body it is probable that the entire investigation of the theorem for eight squares, and the proof that it does not apply beyond that number, will hereafter appear.

It may perhaps be interesting to algebraists to find the real limits to this theorem demonstrably established; and thus to know—in any attempts that may hereafter be made to extend Sir W. R. Hamilton's remarkable and very fertile theory of quaternions—beyond what boundaries such attempts must prove fruitless.

I remain, dear Sir,

Very faithfully yours,

J. R. YOUNG.

Belfast, July 16, 1847.

**XXIV. On the Precipitate produced in Spring and River Waters by Acetate of Lead.** By A. CONNELL, Esq., Professor of Chemistry in the University of St. Andrews\*.

THE white precipitate which it is well known is usually produced in spring and river waters by acetate of lead, has been commonly attributed to the presence of sulphates, chlorides and carbonates. The comparatively trifling action of silver salts, however, shows that it is very rarely, unless in the case of what are called mineral waters, due to chlorides; and the ready solubility of the precipitate in acetic acid in whole or in great part, proves that it is not due to sulphates or phosphates, except in so far as it may be insoluble in acetic acid. Carbonates therefore remain as the probable cause; and this is established by the circumstance, that although effervescence cannot be noticed on the immediate addition of acetic acid, effervescence will be observed if the precipitate is allowed to subside, and the greater part of the solution decanted, and an acid then added. I have found on investigation that carbonate of lime is the usual source of the reaction. The remarkable fact however on this view is, that the reaction is scarcely diminished by boiling and filtering the water; and indeed in some instances does not take place unless these steps are had recourse to, and acetic acid still dissolves the whole or great part. If the waters referred to are boiled and filtered and then largely concentrated by evaporation, they usually deposit carbonate of lime, and do not indicate any such alkaline reaction as shows an alkaline carbonate. The carbonate of lime causing the reaction is therefore evidently held dissolved in the water independently of the presence of free carbonic acid; and I do not think that chemists, generally speaking, are aware that common water may still retain enough of carbonate of lime to give, with acetate of lead, a considerable precipitate of carbonate of lead, although they may have been boiled and filtered. If in any such case the precipitate should be found to dissolve in acetic acid truly *without* effervescence, the probable cause would be the presence of a sufficient quantity of some organic matter, such as crenic or apocrenic acid, which precipitates lead salts; for it is not the least likely that fluorine, which has been found in some spring waters, should ever be present in sufficient quantity to affect lead salts, and fluoride of lead would very likely not be soluble in acetic acid.

The question then arises, whence proceeds this carbonate

\* Communicated by the Author.

of lime. To know whether it arises from the water redis-solving carbonate of lime, which had been held dissolved by carbonic acid and then precipitated by boiling, I transmitted a current of carbonic acid through lime water till it completely redissolved the precipitate which had at first formed. I then boiled the solution for a short time, as in experimenting with the spring waters, and filtered the liquid; but although it was slightly precipitated by acetate of lead, the effect was very much less than that on common water; showing that we cannot account for the effect on common water by supposing that all the carbonic acid had not been driven off by the ebullition. Again, when distilled water was left in contact with marble in impalpable powder for several days, both acetate of lead and oxalate of ammonia showed less lime than in the common waters, although rather more than in the lime-water experiment. I incline therefore to think that the carbonate of lime owes its origin to double decomposition between an alkaline carbonate and a lime salt, such as a chloride. If to a few ounces of distilled water a drop or two of muriate of lime and a drop or two of carbonate of soda be added, the liquid remains quite transparent; and the reaction of common water with acetate of lead and acetic acid may be exactly imitated with this liquid. And in all the common waters yielding the reaction, I could detect alkalies in union with acids.

The common water of the town of St. Andrews, I found, after being boiled and filtered, to yield by evaporation  $\frac{1}{31\frac{1}{2}23}$  of carbonate of lime; and other well and river waters may contain still more. Fresenius has stated that water is capable of holding in solution  $\frac{1}{10601}$  of carbonate of lime, after being saturated with that salt by long-continued boiling, and left in contact for four weeks with the deposit formed on cooling. Nature of course does not take such pains to charge spring waters with lime; and I think the method I have suggested affords a much more simple and probable means of effecting this end.

The St. Andrews' water also contains a trace of carbonate of magnesia after being boiled and filtered; and it is probable that this substance may sometimes be in part the cause of the reaction referred to, but to a much less extent\*.

\* I have given fuller details on this subject in a paper inserted in the Transactions of the Royal Society of Edinburgh for the present year.

*XXV. On the Action of a mixture of Red Prussiate of Potash and Caustic Alkali upon Colouring Matters.* By JOHN MERCER, Esq.\*

A BOUT ten years since I discovered and used extensively in calico-printing the oxidizing properties of a mixture of red prussiate of potash and caustic alkali. For many years I have been in the habit of communicating to my friends several applications of this interesting reaction, among whom I may mention Mr. Crum of Glasgow and Dr. Lyon Playfair. Since then Boudault † has directed attention to the oxidizing power of the same mixture, as far as relates to metallic oxides, but has not shown any important practical application of the knowledge thus acquired.

There are but few processes known in the arts for bleaching indigo, the principal of these being that in which chromic acid liberated from the bichromate of potash by means of an acid is used. In certain cases this process is attended with various disadvantages, and the cloth requires to be subjected to a clearing process to remove the oxide of chromium. The topical application of a mixture of red prussiate of potash and an alkali at once effects the same purpose, and in a most complete manner, leaving a brilliant white on the spot where the colour is discharged without rendering any injury to the fabric. The manner of applying this discharge may be arranged to suit the conditions of the calico-printer. As a class experiment for a lecture-table it is convenient to impregnate the indigo-blue calico with a solution of prussiate of potash, and then dip it into a weak solution of alkali.

This action is a beautiful illustration of those double affinities which we frequently find at play in combinations or decompositions. Thus, though neither chlorine nor charcoal can decompose alumina *per se*, the same gas passed over a mixture of alumina and charcoal combines with the metallic radical; the charcoal in this case having aided the combination by withdrawing the oxygen. It is the same kind of action in the case under consideration. Red prussiate of potash,  $\text{Fe}_2\text{Cy}_6\ 3\text{K}$ , differs from the yellow prussiate,  $\text{Fe}_2\text{Cy}_6\ 4\text{K}$ , by containing one atom less potassium. When potash is presented to the former, this deficient atom of potassium is supplied, but the affinity is not strong enough to liberate the oxygen. When however a second body having an attraction for oxygen, such as litharge or indigo, is presented to the potash and red prussiate, this second affinity

\* Communicated by the Chemical Society; having been read Feb. 1, 1847.

† *Journal de Pharmacie.* [Phil. Mag., vol. xxvii. p. 307.]

acting in a different direction withdraws the oxygen and allows the potassium to unite with the compound radical ferrocyanogen; thus  $\text{Fe}_2\text{Cy}_6\ 3\text{K} + \text{KO} + \text{PbO} = \text{Fe}_2\text{Cy}_6\ 4\text{K} + \text{PbO}_2$ , the decomposition being of the same kind when an organic matter is substituted for the oxide capable of further oxidation. Soda and ammonia may be substituted for potash in the above decomposition, producing the oxidation or discharging the indigo. This is curious in the case of ammonia, for it cannot be explained by any other than by the ammonium theory, and shows the complete analogy between the oxide of ammonium and the oxide of the simple metallic radicals, potassium and sodium. It is interesting also to observe that the last member in the formula  $\text{Fe}_2\text{Cy}_6\ 4\text{R}$ , may be substituted by any alkaline base. Thus, that it may either be  $\text{Fe}_2\text{Cy}_6\ 3\text{K}\ \text{K}$ , or  $\text{Fe}_2\text{Cy}_6\ 3\text{K}\ \text{Na}$ , or  $\text{Fe}_2\text{Cy}_6\ 3\text{K}\ \text{NH}_4$ . This circumstance points to important theoretical considerations in the atomic constitution of the prussiates, which would be foreign to the present paper, the principal object of which is to furnish a means of discharging indigo, and thus supply a process much wanted in the art of calico-printing, and which I have followed for many years with success.

## XXVI. On the Preparation of Hippuric Acid.

By WILLIAM GREGORY, M.D.\*

SINCE the discovery of hippuric acid by Liebig, that body has at all times attracted much attention. Its composition and the products of its decomposition, among which were benzoic acid and benzamide, rendered it interesting, and various ingenious views were entertained of its constitution. Its detection in human urine by Liebig gave it additional importance.

The beautiful discovery of Dessaaignes, that hippuric acid, when heated with strong acids, is resolved into benzoic acid and glycocoll, has greatly increased the interest already attached to hippuric acid, which now affords the best means of obtaining glycocoll, and has enabled Horsford, in his elaborate researches on that substance, to fix its formula in a very satisfactory manner.

If to hydrated hippuric acid . . .  $\text{C}_{18}\text{N}\ \text{H}_9\ \text{O}_6$ ,  
we add 1 equiv. water . . . .  $\text{H}\ \text{O}$ ,  
and from the sum . . . . .  $\text{C}_{18}\text{N}\ \text{H}_{10}\ \text{O}_7$ ,  
subtract 1 equiv. glycocoll . . .  $\text{C}_4\text{N}\ \text{H}_4\ \text{O}_3$ ,  
there remain . . . . .  $\text{C}_{14}\ \text{H}_6\ \text{O}_4$ ,

which is hydrated benzoic acid.

\* Communicated by the Chemical Society; having been read March 15, 1847.

There cannot, I think, be any longer a doubt that  $C_4N\text{H}_4\text{O}_3$  is the true formula of glycocoll, and Horsford has, in establishing this point, at the same time confirmed and explained in the most satisfactory manner the observation of Dessaaignes.

The researches of Horsford, however, have also demonstrated that glycocoll is in itself one of the most interesting compounds known to chemists, and it is evident that the further study of this most singular body will lead to very valuable results.

I have already stated that glycocoll is best obtained from hippuric acid, but as soon as I began to prepare for this purpose a considerable quantity of hippuric acid, I found, as all who have done so must have found, that the operation as prescribed in books is not only tedious and troublesome, but uncertain.

The usual process consists in evaporating the urine of the horse or cow at a moderate temperature to about one-eighth of its bulk, and adding hydrochloric acid, when on standing a few hours, crystals of impure hippuric acid are deposited. But it is well-known that if the temperature should rise too high, although still to a point short of boiling, the hippuric acid will partially or totally disappear, and benzoic acid will be found in its place. Now when we bear in mind that the urine contains but little hippuric acid, it is evident that to obtain this acid in quantity we must operate with a very large bulk of urine, and those who have done so well know how tedious the evaporation is, since if we attempt to hasten it by raising the temperature, we run the risk of losing the whole; and this indeed frequently happens.

The impure, highly-coloured acid first obtained has been purified by different chemists in a great variety of ways. Some have used chloride of lime; but this method is not easily managed, and often converts the whole into benzoic acid.

The last and by far the best method of purification is that of Schwarz, who boils the impure acid with an excess of milk of lime, and strains the alkaline liquid from the undissolved lime. It passes rapidly and clear through calico, and the lime retains the colouring matter, so that the addition of acid to the filtered liquid causes the deposition of crystals of hippuric acid nearly white. Schwarz recommends the addition of chloride of calcium to the filtered or unfiltered liquid, and the precipitation of the lime as carbonate by carbonate of potash or soda, when the precipitated carbonate of lime carries with it the last traces of colouring matter. I have not found this necessary, as a repetition of the process with the milk of lime never fails to yield colourless crystals.

As it was clear that the hippuric acid was not in the slightest degree decomposed by boiling with excess of lime, although so easily metamorphosed by acids, I thought that by applying the same principle to the urine directly, I might be enabled *to boil it down*, and thus shorten the process, and at the same time prevent the decomposition of the hippuric acid, since it would appear that hippurate of lime is not affected by boiling, nor by excess of lime.

Accordingly, I took some urine of the horse, mixed it with excess of milk of lime and boiled for a few minutes. I then strained the solution, which was very materially decolorized, and boiled the clear liquid as rapidly as possible down to the requisite bulk. On adding hydrochloric acid I obtained a copious deposit of crystals, which when pressed had a slight red colour. I then treated them by Schwarz's method and obtained an abundant crop of almost colourless crystals, which consisted entirely of the needles of hippuric acid, without a visible trace of benzoic acid, the crystallization of which is easily recognized. A second treatment with milk of lime, which was hardly needed, and probably would have been quite unnecessary had a greater excess of lime been used in the previous one, yielded snow-white crystals of the utmost beauty and purity.

The improvement which I have thus introduced in the preparation of hippuric acid may seem trifling, and is indeed only the application of Schwarz's method to the urine, instead of to the crude acid; but any one who tries to prepare some ounces, not to say pounds, of hippuric acid, will soon find that the difference is practically important. By my method it is possible to extract in one day the hippuric acid from as much urine as would require a week to operate upon on the usual plan, so that the quantity of hippuric acid which we can thus obtain is only limited, as it were, by the quantity of urine to be procured. The tedious evaporation at low temperatures is got rid of, and we are sure of obtaining the whole hippuric acid originally present; whereas, on the former plan, however carefully the evaporation is conducted, and it requires constant superintendence, it almost always happens that some of the hippuric acid is decomposed; while a very slight accidental rise of temperature may destroy the whole of it, as I have often seen.

On the whole, I am satisfied that all who wish to study hippuric acid and glycocoll will find on trial that what was formerly a disagreeable and troublesome operation is now a very easy and short one; and that they may now easily obtain these remarkable compounds in any desired quantity.

XXVII. *Proceedings of Learned Societies.*

## CAMBRIDGE PHILOSOPHICAL SOCIETY.

[Continued from vol. xxx. p. 367.]

Nov. 9, ON the Structure of the Syllogism, and on the application 1846. of the Theory of Probabilities to Questions of Argument and Authority\*. By Professor De Morgan.

The object of this paper is twofold : first, to establish two distinct theories of the syllogism, both differing materially from that of Aristotle, and each furnishing a general canon for the detection of all its legitimate forms of inference ; secondly, to investigate the mode in which the distinctive character of the two great sources of conviction, *argument* and *authority*, affects the application of the notion of probability to questions not admitting of absolute demonstration.

The two theories of the syllogism arise out of simple notions connected with the *forms* of propositions and their *quantities*. The difference between a positive and negative assertion is not essential, but depends on the manner in which objects of thought are described by language. If *Y* and *y* be names so connected that each contains everything which is not in the other, and the two have nothing in common (a relation which is described by calling them *contrary*)

\* Upon this paper a controversy has arisen, which, up to the present time, may be summed up as follows :—April 30. Mr. De Morgan published a statement in answer to an assertion of Sir W. Hamilton of Edinburgh, to the effect that the second, or quantitative, system of syllogism, was a wilful plagiarism from certain letters which Sir W. Hamilton had written to Mr. De Morgan. May 22. Sir W. Hamilton replied at length in another pamphlet, retracting the assertion of *wilful* plagiarism, but maintaining that the system was taken, unconsciously, from those letters. This was followed by a letter from Mr. De Morgan in the Athenaeum of May 29, and another from Sir W. Hamilton in the same publication for June 5. The point at issue now seems to be as follows :—Mr. De Morgan challenges Sir W. Hamilton to show anything in his second system which was not substantially contained in a digressive section of the description of his first system, admitted to have been sent to Cambridge before any communication had taken place. Sir W. Hamilton, in reply, contends that the digression above-mentioned contains nothing to the purpose. Mr. De Morgan defers further reply until he publishes a work which he states himself to be preparing on logic.

In the Athenaeum of June 19, appeared a letter from Mr. James Broun, asserting certain mistakes on the part both of Sir W. Hamilton and Mr. De Morgan, and giving certain extensions to the quantitative forms of the latter. Again, June 26, appeared in the same publication a letter from Mr. De Morgan, dated June 19, stating that he also had arrived at Mr. Broun's forms, giving reasons for their rejection in favour of certain simpler forms, giving the heads of an extended system of quantitative syllogism, and asserting that he had materially extended both his systems. So the matter stands. The subject of the structure of the syllogism seems to be likely to excite some attention ; and, without pronouncing any opinion on the personal claims or conflicts of the several parties, we recommend the attention of our readers to this rather neglected branch of pure science.—ED. PHIL. MAG.

names), the propositions 'Every X is Y' and 'no X is y' are simply identical. In the same manner, the particular and universal proposition are only accidentally distinct. If in 'some Xs are Ys' the Xs there specified had had a name belonging to them only, say Z, then the preceding proposition would have been identical in meaning with 'every Z is Y.'

From the above it is made to follow, that every legitimate syllogism can be reduced to one of universal affirmative premises, either by introduction of contrary terms, or invention of subgeneric names.

In considering the nature of the simple proposition, Mr. De Morgan uses a notation proposed by himself. Thus—

<i>Every X is Y</i>	is denoted by	X)Y	A
<i>No X is Y</i>	.. ..	X.Y	E
<i>Some Xs are Ys</i>	.. ..	XY	I
<i>Some Xs are not Ys</i>	.. ..	X:Y	O

and names which are contraries are denoted by large and small letters. Aristotle having excluded the contrary of a name from formal logic, and having thereby reduced the forms of proposition to four, these forms (*universal affirmative, universal negative, particular affirmative, particular negative*) the writers on logic in the middle ages represented by the letters A, E, I, O. Thus X)Y and Y)X are equally represented by A. When contraries are expressly introduced, all the forms of assertion or denial which can obtain between two terms and their contraries, are *eight* in number; and the most convenient mode of representing them is as follows:—Let the letters A, E, I, O have the above meaning, but only when the order of subject and predicate is XY. Then let *a*, *e*, *i*, *o* stand for the same propositions, after *x* and *y*, the contraries, are written for X and Y. The complete system then is—

A=X)Y	<i>a=x)y=Y)X</i>
O=X:Y	<i>o=x:y=Y:X</i>
E=X.Y	<i>e=x.y</i>
I=XY	<i>i=xy</i>

and every form in which subject and predicate are in any manner chosen out of the four X, Y, *x*, *y*, so that one shall be either X or *x*, and the other either Y or *y*, is reducible to one or other of the preceding.

The propositions *e* and *i*, which are thus newly introduced, are only expressible as follows, with reference to X and Y.

(i.) *There are things which are neither X nor Y.*

(e.) *There is nothing but is either X or Y or both.*

The connexion of these eight forms is fully considered, and the various syllogisms to which they lead. Rejecting every form of syllogism in which as strong a conclusion can be deduced from a weaker premise; rejecting, for instance,

$$Y)X + Y)Z = XZ$$

because XZ equally follows from Y)X + YZ, in which YZ is *weaker* than Y)Z—all the forms of inference are reduced to three sets.

1. A set of two, called *single* because the interchange of the terms

of the conclusion does not alter the syllogism. Neither of these forms are in the Aristotelian list. One of them is

$$X)Y+Z)Y=xx;$$

or if every X be a Y, and also every Z, then there are things which are neither X nor Z; namely, all which are not Ys.

2. A set of six, in which the interchange produces really different syllogisms of the same form, and in which both premises and conclusion can be expressed in terms of *three names*, without the contrary of either. This set includes the whole Aristotelian list, except those in which a weaker premise will give as strong a conclusion, or the one in which the same premises will give a stronger conclusion.

3. A set of six resembling the last in everything but this, that no one of them is expressible without the new forms *e* and *i*; that is, requiring three names and the contraries of one or more of them.

Those of the third set are not reducible to Aristotelian syllogisms, as long as the eight standard forms of assertion are adhered to.

The second theory of the syllogism has its principles laid down in the memoir before us; but those principles are only applied to the evolution of the cases which are not admitted into the Aristotelian system. The formal statement of the manner in which the ordinary cases of syllogism are connected with those peculiar to this second system is contained in an *Addition*.

In providing that premises shall certainly furnish a conclusion, the common system requires that one at least of the premises shall speak *universally* of the middle term; that is, shall make its assertion or denial of *every* object of thought which is named by the middle term. Mr. De Morgan points out that this is not necessary: *m* being the fraction of all the cases of the middle term mentioned in one premise, and *n* in the other, all that is necessary is that *m+n* should be greater than unity. In such case, the real middle term, being the collection of all the cases by comparison of which with other things inference arises, is the fraction  $m+n-1$  of all the possible cases of the middle term. Thus, from the premises 'most Ys are Xs' and 'most Ys are Zs,' it can be inferred that some Xs are Zs, since *m* and *n* are both greater than one-half. The assignment of definite quantity to the middle term in both premises, gives a canon of inference, of which the Aristotelian rule is only a particular case.

In the addition above alluded to, this same canon, namely 'that more Ys in number than there exist separate Ys shall be spoken of in both premises together,' is made to take the following form:—If in an affirmation or negation, in 'As are Bs' and 'As are not Bs,' definite numerical quantity be given to both subject and predicate, if it be stated how many As are spoken of and how many Bs—the number of *effective* cases of the middle term is seen to be the number of *subjects* in an affirmative proposition, whether the middle term be subject or predicate. Hence, defining the effective number of a premise to be the number of subjects if the proposition be affirmative, and the number of cases of the middle term if it be negative, all that is necessary for inference (over and above the usual condition

that both premises must not be negative) is that the sum of the effective numbers of the two premises shall exceed the number of existing cases of the middle term ; and the excess (being the fraction denoted by  $m+n-1$  in the Memoir) gives the number of cases in which inference can be made.

To attempt to combine these two systems of *form* and of *quantity* is rendered useless by language not possessing the forms of mixed assertion and denial, which the syllogisms deduced from the combination would require. As far as the combination can, in Mr. De Morgan's opinion, be made, nothing is required but a distinct conception of, and nomenclature for, the usual modes of expressing a logical form, and implying one or the other of the alternations which the mere expression leaves unsettled. Mr. De Morgan proposes the following language.

Two names are *identical* when each contains all that the other contains : but when all the first (and more) is contained in the second, then the first is called a *subidentical* of the second, and the second a *superidentical* of the first. Two names are contrary when everything (or everything intended to be spoken of) is in one or the other and nothing in both. But when the two names have nothing in common, and do not between them contain everything, they are called *subcontraries* of one another. And again, if everything be in one or the other, and some things in both, they are called *supercontraries* of one another. Lastly, if the two names have each something in common and something not in common, and moreover do not between them contain everything, each is called a *complete particular* of the other. A table is then given, which contains every form of complex syllogism.

If X and Z be the terms of the conclusion, and both be described in terms of Y, the middle term : it can be seen from this table what can be affirmed and what denied, of X with respect to Z. For instance, if X be supercontrary of Y, and Z subcontrary, then X must be a superidentical of Z : but if X and Z be both subidenticals of Y, nothing can be affirmed ; only it may be denied that X is either contrary or supercontrary of Z.

The remaining part of this paper relates to the application of the theory of probabilities above-mentioned. Mr. De Morgan asserts that no conclusion of a definite amount of probability can be formed from argument alone ; but that all the results of argument must be modified by the testimony to the conclusion which exists in the mind, whether derived from the authority of others, or from the previous state of the mind itself. The foundation of this assertion is the circumstance that the insufficiency of the argument is no index of the falsehood of the conclusion. Various cases are examined ; but it must here be sufficient to cite one or two results.

If  $\mu$  be the probability which the mind attaches to a certain conclusion,  $a$  the probability that a certain argument is valid, and  $b$  the probability that a certain argument for the contradiction is valid : then the probability of the truth of the conclusion is

$$\frac{(1-b)\mu}{(1-b)\mu + (1-a)(1-\mu)}.$$

If  $b=0$ , or if there be no argument against, and if the mind be unbiassed, or if  $\mu=\frac{1}{2}$ , this becomes

$$\frac{1}{2-a} \text{ or } a + \frac{(1-a)^2}{2-a}.$$

For this writers on logic generally substitute  $a$ , confounding the absolute truth of the conclusion with the validity of the argument, and neglecting the possible case of the argument being invalid, and yet the conclusion true.

Nov. 23.—On a New Notation for expressing various Conditions and Equations in Geometry, Mechanics and Astronomy. By the Rev. M. O'Brien.

If  $A, P, P'$  be any three points in space, whether in the same straight line or not, and if the lines  $AP$  and  $AP'$  be represented in magnitude and direction by the symbols  $u$  and  $u'$ , then, according to principles now well-known and universally admitted, the line  $PP'$  is represented in magnitude and direction by the symbol  $u'-u$ . Now if  $AP$  and  $AP'$  be equal in magnitude, and make an indefinitely small angle with each other,  $PP'$  is an indefinitely small line at right angles to  $AP$ , and  $u'-u$  becomes  $du$ . Hence it follows, that, if  $u$  be the symbol of a line of invariable magnitude,  $du$  is the symbol of an indefinitely small line at right angles to it; and therefore, if  $\lambda$  be any arbitrary coefficient,  $\lambda du$  is the general expression for a right line perpendicular to  $u$ .

The sign  $\lambda d$  therefore indicates perpendicularity, when put before the symbol of a line of invariable length. The object of the author is to develope this idea, and to show that it not only leads to a simple method of expressing perpendicularity, but also furnishes a notation of considerable use in expressing various conditions and equations in geometry, mechanics, astronomy, and other sciences involving the consideration of *direction* and *magnitude*.

The author first reduces the sign  $\lambda d$  to a more convenient form, which not only secures the condition that  $u$  is invariable in length, but also defines the magnitude and direction of the perpendicular which  $\lambda du$  denotes. This he does in the following manner. He assumes

$$u = x\alpha + y\beta + z\gamma,$$

(where  $\alpha, \beta, \gamma$  represent three lines, each a unit in length, drawn at right angles to each other, and  $x, y, z$  are any arbitrary numerical coefficients,) and supposes that the differentiation denoted by  $d$  affects  $\alpha, \beta, \gamma$ , but not  $x, y, z$ . This secures the condition that  $u$  is invariable in length, and leads to the following expression for  $\lambda du$ , viz.

$$\lambda du = (zy' - z'y)\alpha + (xz' - x'z)\beta + (yx' - y'x)\gamma,$$

$x', y', z'$  being arbitrary coefficients.

Assuming  $u' = x'\alpha + y'\beta + z'\gamma$ , it appears from this expression for  $\lambda du$ , that  $du = 0$  when  $u = u'$ , and therefore that  $d$  denotes a differential taken on the supposition that  $u'$  is constant.

On this account the author substitutes the symbol  $D_{u'}$  in place of  $\lambda d$ ; he then shows that the operation  $D_{u'}$  is *distributive* with respect to  $u'$  (*i. e.* that  $D_{u'+u''} = D_{u'} + D_{u''}$ ), and to indicate this he elevates

the subscript index  $u'$ , and writes  $Du'.u$  instead of  $D_u u$ . Thus he obtains the expression

$$Du'.u = (zy' - z'y)\alpha + (xz' - x'z)\beta + (yx' - y'x)\gamma.$$

From this it follows that  $Du'.u$  is a line perpendicular both to  $u'$  and  $u$ , and that the numerical magnitude of  $Du'.u$  is  $rr' \sin \theta$ , where  $r$  and  $r'$  are the numerical magnitudes of  $u$  and  $u'$ , and  $\theta$  the angle made by  $u$  and  $u'$ .

Having investigated the principal properties of the operation  $Du'.$ , the author, by a similar method, obtains another notation,  $\Delta u'.u$ , which represents the expression  $xx' + yy' + zz'$ , or  $rr' \cos \theta$ . He then gives some instances of the application of these two notations to mechanics, which may be briefly stated as follows :—

1st. If  $U, U', U'', \&c.$  be the symbols\* of any forces acting upon a rigid body, and  $u, u', u'', \&c.$  the symbols† of their respective points of application, then the six equations of equilibrium are included in the two equations

$$\Sigma U = 0 \text{ and } \Sigma Du.U = 0.$$

2nd. That these two equations are the necessary and sufficient conditions of equilibrium, may be proved very simply from first principles by the use of the notation  $Du$ .

3rd. The theory of couples is included in the equation  $\Sigma Du.U = 0$ . In fact the symbol  $Du.U$  expresses, in magnitude and direction, the axis of the couple by which the force  $U$  is transferred from its point of application  $U$  to the origin.

4th. Supposing that the forces  $U, U', U'', \&c.$  do not balance each other, and putting  $\Sigma U = V, \Sigma Du.U = W$ , we may show immediately, by the use of the notation  $\Delta u$ , that the condition of there being a single resultant is

$$\Delta V.W = 0;$$

and when there is not a single resultant, the axis of the couple of minimum moment is

$$\frac{\Delta V.W}{\Delta V.V} \cdot V.$$

5th. The three equations of motion of a rigid body about its centre of gravity are included in the equation

$$\frac{d}{dt} \left( \Sigma Du \cdot \frac{du}{dt} \delta m \right) = \Sigma Du.U \delta m; \dots \dots \dots \quad (1.)$$

$u$  being the symbol of the position of any particle  $\delta m$  of the body, and  $U$  the symbol of the accelerating force acting on  $\delta m$ .

6th. If  $\omega$  be assumed to represent the expression  $\omega_1\alpha + \omega_2\beta + \omega_3\gamma$ , where  $\omega_1, \omega_2, \omega_3$  are the angular velocities of the planes of  $yz, zx, xy$  about the axes of  $x, y, z$  respectively, then the symbol of the

\* By the symbol of a force is meant the expression  $X\alpha + Y\beta + Z\gamma$ , where  $X, Y, Z$  are the three components of the force.

† By the symbol of a point is meant the expression  $x\alpha + y\beta + z\gamma$ , where  $x, y, z$  are the coordinates of the point.

velocity of  $\delta m$  is  $D\omega.u$ ; from which follow immediately the three well-known equations,

$$\frac{dx}{dt} = \omega_2 z - \omega_3 y, \quad \frac{dy}{dt} = \omega_3 x - \omega_1 z, \quad \frac{dz}{dt} = \omega_1 y - \omega_2 x.$$

The symbol  $\omega$  represents in direction the axis of instantaneous rotation, and in magnitude the angular velocity about that axis.

7th. The equation (1.) may be reduced to the form

$$\frac{d}{dt} \{ A\omega_1\alpha + B\omega_2\beta + C\omega_3\gamma \} = \Sigma Du.U\delta m,$$

which includes Euler's three equations of motion about a fixed point.

8th. If the forces  $U$ ,  $U'$ ,  $U''$ , &c. arise from the attraction of a distant body, the symbol of whose position is  $u'$ , this equation may be further reduced to the form

$$\frac{d}{dt} \left( A\omega_1\alpha + B\omega_2\beta + C\omega_3\gamma \right) = \frac{3m'}{r'^5} Du' \cdot (Ax'\alpha + By'\beta + Cz'\gamma).$$

9th. In the case of the earth attracted by the sun or moon, this equation becomes

$$\frac{d\omega}{dt} = \frac{3m'}{r'^5} \lambda (\Delta u' \cdot \gamma) (Du' \cdot \gamma);$$

$\gamma$  being the polar axis, and  $\lambda = \frac{C-A}{A}$ .

10th. The mean daily motion of  $\gamma$  is given by the equation

$$\frac{d\gamma}{dt} = \frac{3m'}{nr'^5} \lambda (\Delta u' \cdot \gamma) (Du' \cdot \gamma);$$

which equation gives immediately all the well-known expressions for solar and lunar precession and nutation, for  $\frac{d\gamma}{dt}$  is the symbol of the velocity of the north pole, representing that velocity both in magnitude and direction.

Supplement to a Memoir on some cases of Fluid Motion. By G. G. Stokes, M.A., Fellow of Pembroke College, Cambridge.

In a former paper the author had given the mathematical calculation of an instance of fluid motion, which seemed to offer an accurate means of comparing theory and observation in a class of motions, in which, so far as the author is aware, they had not been hitherto compared. The instance referred to is that in which a vessel or box of the form of a rectangular parallelepiped is filled with fluid, closed, and made to perform small oscillations. It appears from theory that the effect of the inertia of the fluid is the same as that of a solid having the same mass, centre of gravity and principal axes, as the solidified fluid, but different principal moments of inertia. In this supplement the author gave a series for the calculation of the principal moments, which is more rapidly convergent than one which he had previously given. It is remarkable that these series, though numerically equal, appear under very different forms, the  $n$ th term of

the latter containing exponentials of the forms  $\varepsilon^{n\pi x}$  and  $\varepsilon^{\frac{n\pi}{x}}$ , while the  $n$ th term of the former contains exponentials of the second form only. In conclusion, the author referred to some experiments which he had performed with a box, such as that described, filled with water, employing the method of bifilar oscillations. The moment of inertia of the fluid about an axis passing through its centre of gravity (*i. e.* the moment of inertia of the imaginary solid which may be substituted for the fluid), was a little greater as determined by experiment than as determined by theory, as might have been expected, since the friction of the fluid was not considered in the calculation. The difference between theory and experiment varied in different cases from the  $\frac{1}{13}$ th to the  $\frac{1}{21}$ st part of the whole quantity.

Dec. 7.—On the Principle of Continuity in reference to certain results of Analysis. By Professor Young of Belfast College.

The object of this paper is to inquire into the influence of the law of continuity, as it affects the extreme or ultimate values of variable functions, more especially those involving infinite series and definite integrals.

The author considers that this influence has hitherto been improperly overlooked; and that to this circumstance is to be attributed the errors and perplexities with which the different theories of those functions are found to be embarrassed. He shows that every particular case of a general analytical form—even the ultimate or limiting case—must come under the control of the law implied in that form; this law being equally efficient throughout the entire range of individual values. Except in the limiting cases, the law in question is palpably impressed on the several particular forms; but at the limits it has been suffered to escape recognition, because indications of its presence have not been actually preserved in the notation.

It is in this way that the series  $1 - 1 + 1 - 1 + \dots$  &c. has been confounded with the limits of the series  $1 - x + x^2 - x^3 + \dots$  &c.; these limits being arrived at by the continuous variation of  $x$  from some inferior value up to  $x=1$ , and from some superior value down to  $x=-1$ . It is shown however that the series  $1 - 1 + \dots$  &c. has no equivalent among the individual cases of  $1 - x + x^2 - \dots$  &c., with which latter, indeed, it has no connexion whatever.

By properly distinguishing between the real limits, and what is generally confounded with them, the author arrives at several conclusions respecting the limiting values of infinite series directly opposed to those of Cauchy, Poisson, and others. And to prevent a recurrence of errors arising from a neglect of the distinction here noticed, he proposes to call such an isolated series as  $1 - 1 + 1 - \dots$  &c. *independent* or *neutral*; and the extreme cases of  $1 - x + x^2 - \dots$  &c., *dependent* series: the difference between a dependent and a neutral series becomes sufficiently marked, as respects notation, by introducing into the former what the author calls the *symbol of continuity*, which indeed is no other than the factor, whose ascending powers Poisson introduces—and, as here shown, unwarrantably—into the successive terms of strictly *neutral* series; thus bringing such series

under the control of a law to which in reality they owe no obedience.

An error somewhat analogous to this is shown to be committed in the treatment of certain definite integrals, which are here submitted to examination and correction, and some disputed and hitherto unsettled points in their theory fully considered. The author is thus led to what he considers an interesting fact in analysis; viz. that the *differentials* of certain forms require *indeterminate corrections*, in a manner similar to that by which *determinate* corrections are introduced into *integrals*; and he attributes to the neglect of these the many erroneous summations assigned to certain trigonometrical series. This is illustrated by a reference to the processes of Poisson.

The paper concludes with some observations on what has been called *discontinuity*; a term which the author thinks is sometimes injudiciously employed in analysis, and prefers to treat discontinuous functions as implying distinct continuities; and by considering these in accordance with the principles established in the former part of the paper, he arrives at results for definite integrals of the form  $\int_{-m}^{+n} x^{-p} dx$  totally different from those obtained by Poisson. Two notes are appended to the paper; one explaining what the author denominates *insensible convergency* and *insensible divergency*, and the other discussing some conclusions of Abel in reference to certain trigonometrical developments.

March 1, 1847.—On the Theory of Oscillatory Waves. By G. G. Stokes, M.A., Fellow of Pembroke College.

The waves which form the subject of this paper are characterized by the property of being propagated with a constant velocity, and without degradation, or change of form of any kind. The principal object of the paper is to investigate the form of these waves, and their velocity of propagation, to a second approximation; the height of the waves being supposed small, but finite. It is shown that the elevated and depressed portions of the fluid are not similar, as is the case to a first approximation; but the hollows are broad and shallow, the elevations comparatively narrow and high. The velocity of propagation is the same as to a first approximation, and is therefore independent of the height of the waves. It is remarkable that the forward motion of the particles near the surface is not exactly compensated by their backward motion, as is the case to a first approximation; so that the fluid near the surface, in addition to its motion of oscillation, is flowing with a small velocity in the direction in which the waves are propagated; and this velocity admits of expression in terms of the length and height of the waves. The knowledge of this circumstance may be of some use in leading to a more correct estimate of the allowance to be made for leeway in the case of a ship at sea. The author has proceeded to a third approximation in the case in which the depth of the fluid is very great, and finds that the velocity of propagation is increased by a small quantity, which bears to the whole a ratio depending on the square of the ratio of the height of the waves to their length.

In the concluding part of the paper is given the velocity of propagation of a series of waves propagated along the common surface of two fluids, of which the upper is bounded by a horizontal rigid plane. There is also given the velocity of propagation of the above series, as well as that of the series propagated along the upper surface of the upper fluid, in the case in which the upper surface is free. In these investigations the squares of small quantities are omitted.

March 15.—Contributions towards a System of Symbolical Geometry and Mechanics. By the Rev. M. O'Brien.

The distinction which has been made by an eminent authority in mathematics between *arithmetical* and *symbolical* algebra, may be extended to most of the sciences which call in the aid of algebra. Thus we may distinguish between *symbolical geometry* and *arithmetical geometry*, *symbolical mechanics* and *arithmetical mechanics*. This distinction does not imply that in one division numbers only are used, and in the other symbols, for symbols are equally used in both; but it relates to the degree of generality of the symbolization. In the arithmetical science, the symbols have a purely numerical significance; but in the symbolical they represent, not only abstract quantity, but also all the circumstances which, as it is expressed, affect quantity. The arithmetical science is in fact the first step of generalization, the symbolical is the complete generalization.

In this view of the case, the author has entitled his paper Contributions towards a System of Symbolical Geometry and Mechanics. The proposed geometrical system consists, first, in representing curves and surfaces, not by equations, as in the Cartesian method, but by *single symbols*; and secondly, in using the *differential notation* proposed in a former paper\* to denote *perpendicularity*, and to express various equations and conditions. The proposed mechanical system is analogous in many respects. Examples of it have already been given in the paper just quoted.

The author uses the term *direction unit* to denote a line of a unity of length drawn in any particular direction; and he employs the symbols  $\alpha \beta \gamma$  to denote any three direction units at right angles to each other.

He defines the position of any point P in space by the symbol representing the line OP (O being the origin) in magnitude and direction. If  $x y z$  be the numerical values of the coordinates of P, and  $\alpha \beta \gamma$  the direction units of the coordinate axes, the expression

$$x\alpha + y\beta + z\gamma$$

represents the line OP in magnitude and direction, and therefore defines the position of P. This expression he calls the *symbol* of the point P.

If  $r$  be the numerical magnitude, and  $\epsilon$  the direction unit of OP, we have

$$r\epsilon = x\alpha + y\beta + z\gamma :$$

$r\epsilon$  is therefore another form for the symbol of the point P.

\* Read Nov. 23, 1846.

The following is the method by which the author represents curves and surfaces.

If the symbol of a point involves an arbitrary quantity, or, as it is called, a variable parameter, the position of the point becomes indeterminate, but so far restricted that it will be always found on some line or curve. Hence the symbol of a point becomes the symbol of a line or curve when it involves a variable parameter.

In like manner, when the symbol of a point involves *two* variable parameters, it becomes the symbol of a surface.

The parameters here spoken of are supposed to be numerical quantities. An arbitrary direction unit is clearly equivalent to two such parameters; and therefore, when the symbol of a point involves an arbitrary direction unit, it becomes the symbol of a surface.

The following are examples of this method :—

1. If  $u$  be the symbol of any particular point of a right line whose direction unit is  $\varepsilon$ , then the symbol of that right line is

$$u + r\varepsilon,$$

$r$  being arbitrary.

2. If  $u$  be the symbol of the centre of a sphere, and  $r$  its radius, the symbol of the surface of a sphere is

$$u + r\varepsilon,$$

$\varepsilon$  being an arbitrary direction unit.

3. If  $u$  be the symbol of any particular point of a plane,  $\varepsilon$  and  $\varepsilon'$  the direction units of any two lines in the plane, the symbol of the plane is

$$u + r\varepsilon + r'\varepsilon',$$

$r$  and  $r'$  being arbitrary.

4. If  $\varepsilon$  be the direction unit and  $r$  the numerical magnitude of the perpendicular from the origin on a plane, the symbol of the plane is

$$r\varepsilon + Dv.\varepsilon,$$

$v$  being an arbitrary line symbol, *i. e.* denoting in magnitude and direction any arbitrary line.

5. If  $u$  and  $u'$  be the symbols of two points, the symbol of the right line drawn through them is

$$u + m(u' - u),$$

$m$  being arbitrary.

6. If  $u$  be the symbol of any curve in space, the symbol of the tangent at the point  $u$  is

$$u + mdu,$$

$m$  being arbitrary.

7. The symbol of the osculating plane at the point  $u$  is

$$u + mdu + m'd^2u,$$

$m$  and  $m'$  being arbitrary.

8. If  $s$  denotes the length of the arc of the curve, and  $\varepsilon$  the direction unit of the tangent, then

$$\varepsilon = \frac{du}{ds}.$$

9.  $\frac{de}{ds}$  or  $\frac{1}{ds} d\left(\frac{du}{ds}\right)$  represents a line equal to the reciprocal of the radius of curvature drawn from the point  $u$  towards the centre of curvature, *i. e.* it represents what may be called the *index of curvature* in magnitude and direction.

Hence, since  $u = x\alpha + y\beta + z\gamma$ , the numerical magnitude of  $\frac{1}{ds} d\left(\frac{du}{ds}\right)$  is

$$\frac{1}{ds} \sqrt{\left\{ \left( d\frac{dx}{ds} \right)^2 + \left( d\frac{dy}{ds} \right)^2 + \left( d\frac{dz}{ds} \right)^2 \right\}},$$

which is the general expression for the reciprocal of the radius of curvature.

10. The symbol of the normal which lies in the osculating plane is

$$u + md\left(\frac{du}{ds}\right),$$

$m$  being arbitrary.

11. The symbol of *any* normal at the point  $u$ , *i. e.* the symbol of the normal plane, is

$$u + Dv.du,$$

$v$  being an arbitrary line symbol.

12. The symbol of the normal perpendicular to the osculating plane is

$$u + mDd^2u.du,$$

$m$  being arbitrary.

13. If  $u$  be the symbol of a surface, involving therefore two variable parameters,  $\lambda$  and  $\mu$  suppose, then the symbol of the normal at the point  $u$  is

$$u + mD \frac{du}{d\lambda} \cdot \frac{du}{d\mu},$$

$m$  being arbitrary.

14. The symbol of the tangent plane at the point  $u$  is

$$u + mdu, \text{ or } u + m \frac{du}{d\lambda} + n \frac{du}{d\mu},$$

$m$  and  $n$  being arbitrary.

15. The symbol of the plane which contains the three points  $u$   $u'$   $u''$  is

$$u + m(u' - u) + n(u'' - u).$$

16. If  $u$  be the symbol of a right line, the symbol of the plane containing it and the point  $u'$  is

$$u + m(u' - u).$$

The following are examples of the proposed mechanical system in addition to those given in the paper already quoted.

1. If  $r$  be the radius vector of a planet, and  $\alpha \beta \gamma$  be chosen so that  $\alpha$  is the direction unit of the radius vector, and  $\gamma$  perpendicular to the plane of the orbit, it may be shown immediately by the sym-

bolical method, that the symbol of the force acting on the planet is

$$\left( \frac{d^2r}{dt^2} - r\omega^2 \right) \alpha + \frac{1}{r} \frac{d(r^2\omega)}{dt} \beta + r\omega\omega'\gamma,$$

where  $\omega$  is the angular velocity of the planet, and  $\omega'$  that of the plane of the orbit about the radius vector. The expressions for the three component forces along  $r$ , perpendicular to  $r$ , and perpendicular to the plane of the orbit, are the coefficients of  $\alpha \beta \gamma$  in this expression.

2. The equation of motion of the planet, when the force is the attraction of a fixed centre varying as the inverse square of the distance, is

$$\frac{d^2u}{dt^2} = - \frac{\mu\alpha}{r^2}.$$

It is curious that this equation is *immediately* integrable, the integral being the two equations

$$r^2\omega = h;$$

$$\frac{h}{r} = \frac{\mu}{h} + e\Delta\beta.\varepsilon.$$

The latter equation is the symbolical equation of a conic section, the origin being focus,  $h$  and  $\varepsilon$  being the arbitrary constants introduced by integration.

3. The application of this method to the case of a planet acted on by a disturbing force is worthy of particular notice, as it expresses the variations of the elements of the orbit with great facility, in the following manner:—

If  $U$  be the symbol of the disturbing force, we have

$$\frac{d(h\gamma)}{dt} = Du.U \quad \dots \dots \dots \quad (1.)$$

$$\frac{d(e\varepsilon)}{dt} = \frac{\mu r}{h^2} \beta\Delta\beta.U + U. \quad \dots \dots \dots \quad (2.)$$

These two equations determine with great facility all the elements of the orbit. For  $\gamma$  is a direction unit perpendicular to the plane of the orbit (*i.e.* it is the symbol of the pole of the orbit), and therefore it defines completely the position of the plane of the orbit. Also  $\varepsilon$  is a direction unit in the plane of the orbit at right angles to the axis major, and therefore it determines the position of the axis major; in fact the direction unit of the axis major is  $D\gamma.\varepsilon$ . The letters  $h$  and  $e$  have their usual signification.

To find  $h$  and  $\gamma$  separately from (1.), suppose that we obtain by integration of (1.)

$$h\gamma = W;$$

then  $h^2 = \Delta W.W$ ; and  $h$  being thus found, we have  $\gamma = \frac{W}{h}$ . The same observation applies to (2.).

4. The expression for the parallax of the planet is

$$\frac{\mu}{h^2} + \Delta\beta \cdot \int dt \left( \frac{\mu r}{h^2} \beta \Delta\beta \cdot U + U \right).$$

These instances suffice to show the nature of the proposed symbolical method.

## ROYAL ASTRONOMICAL SOCIETY.

[Continued from vol. xxx. p. 211.]

April 9, 1847.—On an important error in Bouvard's Tables of Saturn. By Mr. Adams.

Having lately entered upon a comparison of the theory of Saturn with the Greenwich observations, I was immediately struck with the magnitude of the tabular errors in heliocentric latitude, and the more so, since the whole perturbation in latitude is so small, that it could not be imagined that these errors arose from any imperfection in the theory. In order to examine the nature of the errors, I treated them by the method of curves, taking the times of observation as abscissæ, and the corresponding tabular errors as ordinates. After eliminating, by a graphical process, the effects of a change in the node and inclination, a well-defined inequality became apparent, the period of which was nearly twice that of Saturn. One of the principal terms of the perturbation in latitude (viz. that depending on the mean longitude of Jupiter minus twice that of Saturn) having nearly the same period, I was next led to examine whether this term had been correctly tabulated by Bouvard. The formula in the introduction appeared to be accurate; but on inspecting the Table XLII., which professes to be constructed by means of this formula, I was surprised to find that there was not the smallest correspondence between the numbers given by the formula and those contained in the table, the latter following the simple progression of sines, while the formula contained two terms. The origin of this mistake is rather curious. Bouvard's formula for the terms in question is

$$9''\cdot67 \sin\{\phi - 2\phi' - 60^\circ\cdot29\} + 28''\cdot19 \sin\{2\phi - 4\phi' + 66^\circ\cdot12\};$$

but in tabulating the last term he appears to have taken the simple argument  $\phi - 2\phi'$  instead of  $2\phi - 4\phi'$ , so that the two parts may be united into a single term,

$$25''\cdot85 \sin\{\phi - 2\phi' + 43^\circ\cdot88\},$$

which I find very closely to represent Bouvard's Table XLII.

After correcting the above error, and making a proper alteration in the inclinations and place of the node, the remaining errors of latitude are in general very small. I subjoin a correct table to be used instead of Bouvard's. The constant added being  $36''\cdot0$  instead of  $26''\cdot0$ , it will be necessary to subtract  $10''\cdot0$  from the final result.

Table XLII.—Argument III. de la Longitude.

Argument.	Equation.	Argument.	Equation.	Argument.	Equation.	Argument.	Equation.
0	52·4	2500	17·4	5000	68·1	7500	6·1
100	54·4	2600	16·2	5100	69·4	7600	4·0
200	56·0	2700	15·5	5200	70·2	7700	2·3
300	57·2	2800	15·2	5300	70·5	7800	1·1
400	58·0	2900	15·2	5400	70·4	7900	0·4
500	58·3	3000	15·7	5500	69·8	8000	0·1
600	58·3	3100	16·6	5600	68·7	8100	0·4
700	57·8	3200	17·9	5700	67·2	8200	1·0
800	56·9	3300	19·6	5800	65·3	8300	2·2
900	55·7	3400	21·7	5900	62·9	8400	3·7
1000	54·1	3500	24·1	6000	60·1	8500	5·7
1100	52·2	3600	26·7	6100	57·1	8600	8·0
1200	50·0	3700	29·7	6200	53·7	8790	10·7
1300	47·5	3800	32·8	6300	50·0	8800	13·7
1400	44·9	3900	36·2	6400	46·2	8900	16·8
1500	42·1	4000	39·6	6500	42·1	9000	20·2
1600	39·2	4100	43·1	6600	38·0	9100	23·7
1700	36·2	4200	46·5	6700	33·9	9200	27·3
1800	33·3	4300	50·0	6800	29·8	9309	31·0
1900	30·4	4400	53·3	6900	25·7	9400	34·5
2000	27·7	4500	56·5	7000	21·8	9500	38·0
2100	25·1	4600	59·4	7100	18·1	9600	41·4
2200	22·8	4700	62·1	7200	14·6	9700	44·6
2300	20·6	4800	64·5	7300	11·4	9800	47·5
2400	18·8	4900	66·5	7400	8·5	9900	50·1
2500	17·4	5000	68·1	7500	6·1	10000	52·4

Constante ajoutée 36"·0.

## On the Development of the Disturbing Function R. By Sir John Lubbock.

The greatest practical difficulty which is encountered in the planetary theory consists in the development of the expression for the reciprocal of the linear distance between the disturbed and disturbing planets. The algebraical expression of this development may be obtained either by means of the binomial theorem or by Taylor's theorem applied to several variables; by the latter method M. Binet has carried the development as far as terms of the 7th order. But when high powers of the eccentricities and inclinations are retained, the expressions become excessively complicated, so that further progress in this direction appears utterly hopeless.

The numerical coefficients of the series may also be obtained by quadratures; but to determine all the coefficients in this way would involve very great labour.

In considering the problem of the perturbations of bodies whose eccentricities and inclinations are considerable, the author has been led to another mode of development, which he conceives to possess great advantages over those just mentioned, and the use of which may be greatly facilitated in all cases by special tables, which may be prepared beforehand.

The principle of this method consists in expressing the square of the ratio of the distance between the two planets to the radius vector of the more distant planet, under the form of  $P - Q$ , in which  $P$  is the product of any convenient number of factors of the form  $1 + A \cos \alpha$ , and all the terms in  $Q$  have small coefficients. Then  $(P - Q)^{-\frac{1}{2}}$  may be developed by the binomial theorem in a series of ascending powers of  $Q$ , which consequently converges rapidly, and the values of the quantities  $P^{-\frac{1}{2}}$ ,  $P^{-\frac{3}{2}}$ , &c., which enter into the successive terms of this series, may be found by multiplying together the developments of the several factors  $(1 + A \cos \alpha)^{-\frac{1}{2}}$ ,  $(1 + A \cos \alpha)^{-\frac{3}{2}}$ , &c. If then tables were prepared, giving for different values of  $A$  the coefficients of the development of these quantities in cosines of multiples of  $\alpha$ , all the operations requisite for the development of the disturbing function might be performed with great facility.

The author remarks, in conclusion, that instead of developing, as is usually done, in powers of the ratio of the mean distances  $\left(\frac{a}{a'}\right)$ , it would be preferable to develop according to powers of  $\frac{a}{\sqrt{a^2 + a'^2}}$ , which is much less than the former when  $a$  and  $a'$  do not differ widely from each other.

Observations of Hind's Second Comet in full Sunshine\*. By Mr. Hind.

I take the liberty to send you two positions of the comet discovered here Feb. 6, obtained yesterday in full daylight, and about five hours before the perihelion passage. The visibility of a comet in the daytime, and within  $2^\circ$  distance from the sun, is a phenomenon of so rare occurrence, that it may in some measure interest you if I give very briefly the particulars of our observations.

I had determined, by theory, that the intensity of light on March 30 ought to be 100 times stronger than that of a star of fourth magnitude, and was induced to make preparations for a daylight observation. I first saw the comet about 11 A.M. When the sky was perfectly cloudless about the sun, it had a whitish appearance, which rendered it a matter of no little difficulty to see the comet; but during the passage of some cumuli clouds over the sun, and between the breaks, I obtained some excellent views of the comet, and several observations, which will no doubt be of great assistance in the accurate determination of the elements. The nucleus was nearly, if not perfectly, round, beautifully defined and planetary, the diameter  $8''$  or  $10''$ . Two faint branches of light formed a divided tail, extending about  $40''$  from the head, like two longish erect ears or horns rising from each side of the disc. At times I felt certain that the nucleus twinkled. The tail resembled a thin smoke.

With respect to the observations for position, I can only add that they were as good as could possibly be made, under the circum-

\* The comet was seen at noon near the sun by two other observers, at Truro and in the Isle of Anglesey.

stances, by instrumental comparisons. The index errors are very constant, and were accurately determined last evening.

	Greenwich M.T. h m s	Comet's R.A. h m s	Comet's Dec. +° ′ ″	Weight.
March 30	1 23 40	7 32 27	+1 48 42	1
	1 55 8	7 33 56	+1 45 21	2

In the observations for the first position the centre of the field was estimated, and nine single results are tolerably accordant. The second place depends on one good observation with cross wires, clouds preventing any further comparisons.

Had the sky been free from the whiteness which is so fatal to vision by daylight, I should have obtained much better places.

I communicated an ephemeris to Mr. Dawes, who has observed the comet with extreme care, but I do not know at present whether he saw it yesterday in daylight.

### *XXVIII. Intelligence and Miscellaneous Articles.*

**ON A NEW TEST FOR PRUSSIC ACID, AND ON A SIMPLE METHOD OF PREPARING THE SULPHOCYANIDE OF AMMONIUM. BY PROF. LIEBIG.**

WHEN some sulphuret of ammonium and caustic ammonia are added to a concentrated aqueous solution of prussic acid, and the mixture heated with the addition of pure flowers of sulphur, the prussic acid is converted in a few minutes into sulphocyanide of ammonium. This metamorphosis depends on the circumstance, that the higher sulphurets of ammonium are instantly deprived by the cyanide of ammonium of the excess of sulphur they contain above the monosulphuret; for instance, if a mixture of prussic acid and ammonia be added to the pentasulphuret of ammonium, the solution of which is of a deep yellow colour, and the whole gently heated, the sulphuret of ammonium is soon decolorized; and when the clear colourless liquid is evaporated, and the admixture of sulphuret of ammonium expelled, a white saline mass is obtained, which dissolves entirely in alcohol. The solution yields, on cooling or evaporation, colourless crystals of pure sulphocyanide of ammonium. Only a small quantity of sulphuret of ammonium is requisite to convert, in the presence of an excess of sulphur, unlimited quantities of cyanide of ammonium into sulphocyanide; because the sulphuret of ammonium, when reduced to the state of monosulphuret, constantly reacquires its power of dissolving sulphur and transferring it to the cyanide of ammonium. The following proportions will be found to be advantageous:—2 oz. of solution of caustic ammonia of 0·95 spec. grav. are saturated with sulphuretted hydrogen gas; the hydrosulphate of ammonia thus obtained is mixed with 6 oz. of the same solution of ammonia, and to this mixture 2 oz. of flowers of sulphur are added; and then the product resulting from the distillation of 6 oz. prussiate of potash, 3 oz. of the hydrate of sulphuric acid, and 18 oz. water. This mixture is digested in the

water-bath until the sulphur is seen to be no longer altered and the liquid has assumed a yellow colour; it is then heated to boiling, and kept at this temperature until the sulphuret of ammonium has been expelled and the liquid has again become colourless. The deposited, or excess of, sulphur is now removed by filtration, and the liquid evaporated to crystallization. In this way from  $3\frac{1}{2}$  to  $3\frac{1}{2}$  oz. of dazzling white dry sulphocyanide of ammonium are obtained, which may be employed as a reagent, and for the same purposes as the sulphocyanide of potassium. Of the 2 oz. of sulphur added,  $\frac{1}{2}$  an oz. is left undissolved.

The behaviour of the higher sulphurets of ammonium towards prussic acid furnishes an admirable test for this acid. A couple of drops of a prussic acid, which has been diluted with so much water that it no longer gives any certain reaction with salts of iron by the formation of prussian blue, when mixed with a drop of sulphuret of ammonium and heated upon a watch-glass until the mixture is become colourless, yields a liquid containing sulphocyanide of ammonium, which produces with persalts of iron a very deep blood-red colour, and with persalts of copper, in the presence of sulphurous acid, a perceptible white precipitate of the sulphocyanide of copper.

—Liebig's *Annalen*, Jan. 1847.

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#### ON THE FUSION OF IRIDIUM AND RHODIUM. BY R. HARE.

This communication respects mainly my success in fusing both iridium and rhodium, neither of which, in a *state of purity*, had been previously fused. It may be supposed that the globule of iridium, obtained by Children's colossal battery, forms an exception; but the low specific gravity and porosity of that globule may justify a belief that it was not pure, and at any rate the means employed were of a nature not to be at command for the repetition of the process, so that iridium might as well be infusible, as to be fusible only by such a battery.

The first specimen of the last-mentioned metal on which I operated was one given me by Mr. Booth, a former pupil of Wöhler, whom he had assisted in obtaining it by the excellent process devised by that distinguished chemist. This specimen was fused in the presence of Mr. Booth. Subsequently I procured specimens, warranted pure, severally from the house of Pelletier at Paris, and from Messrs. Johnson and Cock, London. Another specimen was given to me by a friend, who had received it as pure, from a source on which reliance may be placed; and lastly, I obtained myself, by Wöhler's process, a specimen of about sixty grains, from the insoluble residue of platinum ore. All the specimens thus procured were found to be fusible under my hydro-oxygen blowpipe. The specimen obtained from Messrs. Johnson and Cock, after repeated fusions, by which it was much consolidated, weighed sixty-seven grains. During fusion there appeared to be an escape of volatile matter, supposed to be osmic acid, arising from the presence of a minute portion of osmium, between which and iridium an affinity of

a peculiar degree of energy exists. At a certain point of the process a reaction took place sufficiently explosive to throw a portion of the metal, in globules, off from the support. One of these, about twice as large as the head of a common brass pin, proved to be hollow. By prolonged and repeated fusion the metal became more compact and more fusible.

Fused iridium has nearly the grain of soft cast steel, with the pale whiteness of antimony, and appears to be susceptible of a fine polish. Although as hard as untempered steel, it is somewhat sectile, since, when split by means of a cold chisel, the edge penetrated about the eighth of an inch before a division was effected. By light hammering a corner was flattened without fracture, although under heavier blows the mass cracked. I infer that although nearly unmalleable and very hard, iridium may be wrought in the lathe.

I have already mentioned that I fused into a globule a specimen of iridium obtained by me from the insoluble residuum of platinum ore by Wöhler's process. From this globule, while congealing, a portion ran out from the inside, leaving a cavity and covering one of its sides externally with an incrustation, among which crystalline spangles, or facets, were discernible. The specific gravity of the globule of iridium, from the specimen furnished by Messrs. Johnson and Cock, was taken by Mr. T. R. Eckfelt of the United States mint at Philadelphia, and by Dr. Boyé, both having balances of the greatest accuracy, and being very skilful in the employment of them. In the first instance there was a perfect coincidence in the results obtained, 21·83 being the numbers found by both of these gentlemen. Agreeably to another trial made by Dr. Boyé, using river-water instead of distilled, the number was 21·78, water being in either case about sixty-eight, with allowance for the difference of the water, and the temperature being above the standard of 60°. The specific gravity of the specimen may then be estimated at 21·80.

The specific gravity of fused platinum, purified according to the instructions of Berzelius, before subjection to the hammer, proved in one specimen to be not more than 19·70, although by hammering it became equal to 21·23. It is with fused platinum that fused iridium should be compared. Of course the specific gravity of the last-mentioned metal, when both are obtained by fusion, may be assumed to be one-tenth greater than that of the former. Moreover, as this metal is the only impurity existing in the standard platinum of London, of Paris, or of St. Petersburg, it follows that a high specific gravity is not to be viewed as a proof of purity. Accordingly a specimen of platinum, purified from iridium by the Berzelian process, and which had proved eminently susceptible of being beaten into leaf, was found only to be of the gravity of 21·16, while that of a specimen of standard Russian platinum, very brilliantly white but inferior in malleability, presented to me by his Excellency Count Cancrine, as a specimen of the purest platinum of the Russian mint, was 21·31.

Of rhodium I have fused two specimens, one of five pennyweights, purchased of Messrs. Johnson and Cock, the other received through

the same channel as the specimen of iridium above-mentioned\*. Rhodium is at least as fusible as iridium, both of the specimens alluded to having been converted into fluid globules. That procured from Messrs. Johnson and Cock gave a globule weighing ninety grains. On a second fusion it formed a perfect globule as fluid as mercury; and yet in congealing lost its brilliancy by becoming studded with crystalline facets all over its surface, excepting the portion in contact with the support. The facets had the appearance of incipient spangles. The rapidity with which they were formed seemed anomalous. The mass being split by a cold chisel and viewed by a microscope, it appeared porous immediately beneath the facets. When the mass was first fused, I found by the gravimeter the specific gravity to be 11·0, which coincides with the observations of Wollaston. Yet by a careful trial made at the United States mint by Mr. Eckfelt, after the second fusion and the formation of the facet, the specific gravity proved to be only 10·8. This is sufficiently explained by the porosity above mentioned. In fact the porosity to which rhodium and iridium are liable may render it difficult to find specimens of precisely the same specific gravity.

In sectility, malleability and hardness, rhodium did not appear to differ much from iridium, but it is not of so pale a white as iridium. The one has the pale white of antimony, the other the ruddy hue of bismuth.

Osmiuret of iridium, as existing in the native spangles associated with platina ore, or as otherwise obtained, is far more difficult of fusion than pure iridium. The propensity to assume the crystalline form, and to adhere to it, is even greater in this alloy than in the last-mentioned metal. On first exposure to the most intense heat of the hydro-oxygen blowpipe some slight appearances of fusion may be seen, and the spangles or grains may be made to cohere. Nevertheless it yields very slowly, and requires an expenditure of gas too great to be incurred unless it were for the purpose of once well determining the question of its ultimate fusibility. This object was obtained completely as respects a globule of 45 grains in weight. The specific gravity of this globule appeared to be 20·4, but this result was evidently less than that which would have been obtained had there not been some minute cavities, which, after splitting the globule, were detected by a magnifier.

The specific gravity of some large spangles of osmiuret of iridium from South American ore was, by Dr. Boyé, found to be 19·835. That of some grains heavier but not so flat, presented to me by Count Cancrine, was found to be 20·938.

That the alloy of iridium with osmium should be more difficult to fuse than pure iridium, leads to the inference that osmium must be the most infusible of the metals, although, like carbon, very susceptible of combustion, and capable, like that infusible non-metallic radical, of forming a volatile peroxide. Of course its liability to oxidizement would render it impossible to fuse it by the hydro-

\* One other larger specimen from the same source has been fused since the above was written.

oxygen blowpipe, of which the efficacy requires the simultaneous presence of oxygen and the most intense heat. It might be fused by exposure *in vacuo* to the discharge of a powerful voltaic series, by means of the apparatus of which a description with engravings has been given in a recent volume of the Transactions of the American Philosophical Society, and republished in 'Silliman's Journal' for 1841, vol. xl. p. 303.

I have obtained osmium by heating the osmiate of ammonia in a glass tube with sal-ammoniac, agreeably to the instructions given by Berzelius. In this way a result was obtained which the information given by that distinguished chemist had not led me to anticipate. The tube became coated with a ring of osmium, which it would be impossible by inspection merely to distinguish from the arsenical ring on the peculiar features of which reliance has been placed for the detection of arsenic.

It follows from my experiments and observations, that of all metallic bodies, osmiuret of iridium is the most difficult to fuse; that rhodium and iridium are both fusible by the hydro-oxygen blowpipe, properly employed; that the former has the rosy whiteness of bismuth, the latter the pale white of antimony; and that both of them are slightly sectile, though extremely hard and nearly un-malleable; that iridium *merely fused* is heavier than platinum *condensed by the hammer*. Thus it follows from my experiments, and from the recent observations of Breithaupt, on some specimens of native iridium, that the metal, whether in this state or pure as obtained by chemical skill and consolidated by fusion, must be allowed that pre-eminence in density, which, until of late, was given to platinum.

It may be proper to add, that subsequently to the writing of the preceding narrative, receiving some large quantities of iridium and rhodium from Messrs. Johnson and Cock, my experiments were successfully repeated on a larger scale, but without any result besides that of confirming the facts above stated.—*Silliman's Journal for Nov. 1846*, p. 365.

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NOTE ON THE MEANS OF TESTING THE COMPARATIVE VALUE  
OF ASTRINGENT SUBSTANCES FOR THE PURPOSES OF TAN-  
NING. BY ROBERT WARINGTON, ESQ.

Having been frequently called upon to examine the value of astringent substances imported into this country for the purposes of tanning, such as valonia, divi-divi, sumac, cutch, &c., I am induced to believe that the detail of the manipulation adopted may not be without interest to some of the members of the Society. As the manufacture of leather was the object of the purchaser of these materials, gelatin was selected as the basis for the estimation of their comparative value; and after several trials with various kinds of natural and manufactured gelatin, such as varieties of isinglass, glue, patent gelatin, &c., the finest long staple isinglass was found to be the most constant in its quality and least liable to undergo change.

With this therefore the test solution was prepared, of such a strength, that each division, by measure in the ordinary alkalimeter tube, should be equivalent to the one-tenth or one-fourth of a grain of pure tannin, and thus the number of divisions used would indicate the proportion of available tannin or substance precipitable by gelatin contained in any specimen. A given weight of the sample under trial was then infused in water, or if necessary the astringent matter extracted by boiling, and the clear liquid precipitated by the test solution until no further deposit occurred.

It was necessary in the course of this operation to test at intervals a portion of the solution under examination, to ascertain the progress of the trial ; and this, from the nature of the precipitate, was attended at first with some little difficulty : paper filters were inadmissible from the quantity of the solution they would absorb, and thus introduce a source of extensive error ; subsidence rendered the operation very tedious. The plan I have adopted is as follows :—a piece of glass tubing, about twelve inches in length and about half an inch internal diameter, is selected, and this has a small piece of wet sponge loosely introduced into its lower extremity, and when it is wished to abstract a part of the fluid under investigation for a separate testing, this is immersed a few seconds in the partially precipitated solution ; the clear liquid then filters by ascent through the sponge into the tube, and is to be decanted from its other extremity into a test glass ; if on adding a drop of the gelatin solution to this a fresh precipitate is caused, the whole is returned to the original bulk, and the process proceeded in, and so on until the operation is perfected ; this method of operating is facilitated by conducting the examination in a deep glass. After a few trials the manipulation will be found extremely easy, and in this way considerable accuracy may be arrived at.—*From the Proceedings of the Chemical Society.*

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**ON THE TWO VARIETIES OF ARSENIOUS ACID. BY M. BUSSY.**

The author first gives a new process for determining the quantity of arsenious acid. This process is based on the employment of standard reagents. The reagent which he uses is permanganate of potash, which M. Marguerite has already successfully employed for the quantitative determination of iron.

When a solution of permanganate of potash is poured into a solution of arsenious acid, it becomes arsenic acid, and the red colour of the reagent disappears. The liquor begins to become coloured only when the transformation of arsenious acid is complete. When, then, a standard solution of permanganate of potash is prepared, the quantity of arsenious acid contained in any solution may be determined by that of the permanganate required to convert it into arsenic acid.

M. Bussy states that the two varieties of arsenious acid, the vitreous and opake, absorb the same quantity of permanganate, and consequently that the differences observed in their solubility is not derived from any difference of oxidizement.

With respect to the solubility of the two varieties of arsenious

acid, M. Bussy has arrived at the following conclusions :—1st. The vitreous, so far from being less soluble in water than the opake acid, as stated by chemists, is, on the contrary, much more soluble. This difference is nearly in the proportion of 3 to 1, at about  $53^{\circ}$  to  $55^{\circ}$  of F.; the same quantity of water which dissolves 36 to 38 parts of the vitreous acid, will take up only 12 to 14 of the opake. 2nd. The vitreous acid dissolves much more rapidly than the opake acid. 3rd. Neither of the varieties possesses a degree of solubility which is to be regarded as strictly peculiar to it. 4th. The opake acid is converted into vitreous acid by long boiling in water; that is to say, it then acquires the same degree of solubility as the vitreous arsenious acid, which is such that 11 parts are dissolved by 100 of water. 5th. Under the influence of water and a low temperature, the vitreous acid is converted into opake acid; that is to say, a solution of vitreous acid becomes reduced after a certain time to the point of saturation which belongs to the opake acid. 6th. The mixture of the two varieties of acid in the same solution explains the anomalies observed in the solubility of arsenious acid, which in fact offers nothing opposed to the principles admitted by chemists. 7th. Division, which facilitates the solution of the opake acid, without however increasing its solubility, considerably diminishes that of the vitreous acid; and to such an extent, that this acid, reduced to fine powder and levigated, is not sensibly more soluble in water than the opake acid; this resulting unquestionably from a transformation which it undergoes, either at the moment of pulverization, or of its contact with water. 8th. Acid which has been rendered opake by the action of ammonia, and acid crystallized in water, act similarly with water, and appear to belong to the same variety. 9th. The opake acid dissolves more slowly than the vitreous in dilute hydrochloric acid. This circumstance, which thus modifies the nature of the products formed during solution, explains why the luminous phenomena observed by M. Rose in the crystallization of the vitreous acid, are not in general observable with so great intensity in the solution of the opake variety. 10th. The difference which has been observed in the action of the two arsenious acids on tincture of litmus is merely apparent. If the opake acid does not reddens the tincture, it is on account of its slight solubility, and especially because it dissolves slowly; whilst the vitreous acid, which dissolves quickly, immediately reddens the tincture. But if comparative experiments be made, and the tincture be exposed to the action of the powder, it becomes gradually red, and no difference is perceptible at the expiration of three or four days.—*Comptes Rendus*, Mai 1847.

#### ON THE PREPARATION OF GUN-COTTON.

Mr. Coathupe recently forwarded to the Chemical Society two specimens of gun-cotton, with a view to illustrate the greatly increased explosive effects that are to be derived from a subsequent immersion of the gun-cotton, when properly prepared in the ordinary way, in a saturated solution of chlorate of potash.

" Having experimented with solutions of nitrate of ammonia, nitrate of potash, nitrate of soda, bichromate of potash, &c. &c., for the purpose of increasing the explosive properties of this interesting substance, I can affirm that none of the results will bear the slightest comparison with those obtained from the solution of chlorate of potash, either in rapidity of ignition or in intensity of flame. The process adopted for preparing the inclosed specimens was as follows : viz. into a mixture of equal measures of strong *nitrous* acid and of oil of vitriol, spec. grav. 1·845, the cotton was immersed and stirred with a glass rod during about three minutes : it was then well-washed in many waters and dried ; a portion of it was then soaked for a few minutes in a saturated solution of chlorate of potash, well-squeezed and dried."

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#### ON BALSAM OF TOLU, AND SOME PRODUCTS DERIVED FROM IT.

M. E. Kopp states that the experiments which he has made on this substance confirm the greater number of the results previously obtained. He remarks that the balsam is composed of a very small quantity of tolene  $C^{10} H^{16}$ ,  $C=75$   $H=6\cdot25$  ; of free cinnamic acid,  $C^{18} H^{16} O^4$  ; of a resin very soluble in alcohol,  $C^{36} H^{58} O^8$  ; of a resin slightly soluble in alcohol,  $C^{18} H^{20} O^5$ , or  $C^{36} H^{40} O^{10}$ .

*Tolen.*—This carburetted hydrogen was prepared by exactly following the plan proposed by M. Deville. It is colourless, very fluid, of a penetrating taste somewhat like pepper, and its smell resembles that of elemi. Its density at 60° F. is 0·858 ; its boiling-point is between 310° and 320° F. Exposed in an imperfectly closed tube, it gradually becomes resinous and very slightly coloured. M. Deville gives as its formula  $C^{12} H^{18}$ . M. Kopp states that his analysis, which differs but little from that of M. Deville, indicates  $C^{10} H^{16}$ .

*Cinnamic Acid.*—The free acid of balsam of Tolu, as observed by M. Fremy, is merely cinnamic acid. This fact was proved by analysis, and by its conversion into nitrocinnamic acid, very slightly soluble in cold alcohol ; whereas benzoic and nitrobenzoic acids are very soluble in it. The results obtained by M. Deville are probably derived from his having examined the acids procured by the distillation of the balsam, or extracted by concentrated alkaline solutions.

M. Kopp has shown that, under these two circumstances, the resins of balsam of Tolu are so changed as to give rise to a large proportion of benzoic acid. The resins, cautiously distilled with caustic soda, yield pure benzoe, and a coaly residue which contains much benzoate of soda. Cinnamic acid, mixed with cold concentrated caustic soda, and submitted to a current of chlorine, is converted into chlorocinnamic acid  $C^{18} (H^{14} Cl^2) O^4$ . If however the temperature be raised and the action is very strong, the chlorinated oil described by Mr. Stenhouse is disengaged, and chlorobenzoic acid,  $C^{14} (H^{10} Cl^2) O^4$ , is formed.

These two acids strongly resemble each other ; but the latter is more soluble in water and in alcohol, and its salts crystallize more readily. Cinnamic acid, treated with concentrated nitric acid, is at

first converted into nitrocinnamic acid, then into benzoic acid, and finally into nitrobenzoic acid.

Cinnamic and benzoic ethers are both, though with great difficulty, converted into nitrocinnamic acid and nitrobenzoic ether. There is almost always a great part of the ether decomposed, and the acids are set free.

Nitrobenzoic ether is solid, colourless, and of an aromatic odour and taste. It crystallizes in fine rhombic laminae. Its melting-point is  $116^{\circ}$ , and its boiling-point  $564^{\circ}$ . It is easily obtained by exposing an alcoholic solution of nitrobenzoic acid to a current of hydrochloric acid gas. Its formula is  $C^{14} (H^8 N^2 O^4) O^3 + C^4 H^{10} O = C^{18} H^{18} N^2 O^5$ .

Nitrocinnamic acid dissolved in an alcoholic solution of sulphuret of ammonia is reduced with the assistance of a gentle heat. Sulphur is deposited, and two distinct substances are formed, one of which is of a yellowish colour and belongs to the class of resins, and the other to that of alkaloids. The latter is solid, colourless, crystallizes in small indistinct masses, insoluble in water, soluble in alcohol and in ether, and forms difficultly crystallizable salts.

*Resin  $\alpha$* ,  $C^{36} H^{38} O^8$ . This substance is brown, translucent, brittle when cold; its powder agglomerates at  $59^{\circ}$  F. and fuses perfectly at  $140^{\circ}$  F. Concentrated sulphuric acid imparts a purple colour to it. When dissolved in potash and exposed to the air, it is readily oxidized, and is converted into resin  $\beta$ . By dry distillation it yields benzoen and benzoic acid. It dissolves readily in alcohol and in ether.

*Resin  $\beta$* ,  $C^{18} H^{20} O^5$ . Colour dull brownish-yellow, without taste or smell, slightly fusible (above  $212^{\circ}$  F.), but little soluble in alcohol or ether. It is less alterable than the preceding resin. Sulphuric acid renders it of a violet colour; potash dissolves it with a brown colour.

The mixture of the two resins treated with nitric acid yields, as gaseous products, carbonic acid, nitrous vapours and nitric oxide; as volatile products, hydruret of benzole, hydrocyanic acid, and a little benzoic acid; as residue, a flocculent yellowish substance, which is benzoic acid intimately combined with a yellow colouring matter of a resinous nature, which destroys its crystallizing power, and accompanies it in all its combinations, even in that of ether. By the action of heat, especially by distillation, the resinous matter is destroyed, and perfectly pure benzoic acid is obtained. The resin yields nearly one-third of its weight of benzoic acid.

As to the constitution of balsam of Tolu, it seems very simple. Primarily it is formed of the soft resinous matter  $C^{36} H^{38} O^8$ , or of that which gives rise to it. This resin, under the influence of the air, is converted into cinnamic acid and resin  $\beta$ :  $C^{36} H^{38} + O^2 = C^{18} H^{16} O^4 + C^{18} H^{20} O^5 + H^2 O$ . In fact it is observed that in time balsam of Tolu becomes hard, and contains a larger quantity of cinnamic acid. The resin  $C^{18} H^{20} O^5$  may itself easily furnish benzoic acid for  $C^{18} H^{20} O^5 = C^{14} H^{12} O^4 + H^2 O + C^4 H^4$ . The carburetted hydrogen perhaps gives rise to tolene; but it is more probable that it is converted by the action of oxidizing bodies into resinous colour-

ing matter, or perhaps into water and carbonic acid.—*Ann. de Ch. et de Phys.*, Juillet 1847.

**ON THE EQUIVALENT OF TITANIUM. BY M. ISIDORE PIERRE.**

The author remarks that chemists generally agree that it would be difficult to add to the precision of the numbers which represent the equivalents of hydrogen, carbon, chlorine, bromine, iodine, phosphorus, arsenic and silicon, as determined by the researches of Dumas, Marignac and Pelouze.

M. Pierre thinks however that this is not the case with titanium; and that if the labours of different periods respecting this substance be examined, it will be evident that its equivalent requires renewed examination.

M. H. Rose originally obtained, by various methods, numbers which varied between 380 and 450; but he afterwards found that the sulphuret of titanium which he employed in his experiments, was procured free from titanic acid with great difficulty.

In his last experiments, M. Rose made use of chloride of titanium, which he decomposed by water. He precipitated with ammonia the titanic acid derived from this decomposition, and afterwards treated the filtered liquor with nitrate of silver, in order to separate the chlorine in the state of chloride of silver: this method gave him 303·686 as the equivalent of titanium.

The chloride of titanium used by M. Pierre was not prepared from rutile, but from calcined artificial oxide of titanium: it was free from oxide of iron and from chloride of silicium, and its boiling-point was perfectly stationary. The chloride employed had been kept in a small tube from the time of its preparation hermetically sealed: it was broken by agitation in a stopped bottle, one quarter filled with distilled water. By frequent agitation, without unstopping the bottle, the whitish cloud at first produced above the liquid disappears. Without this precaution there would be a probable loss of hydrochloric acid in opening the bottle too soon, or by introducing the solution of silver, which would expel a small quantity of this vapour.

The following results were obtained:— gr.

I. Chloride of titanium employed..	0·8215
Silver .....	1·84523
indicating Chlorine .....	0·60623
Titanium by difference.....	0·21727

These results gave 314·76 as the equivalent of titanium.

II. Chloride of titanium employed..	0·774
Silver.....	1·73909
indicating Chlorine.....	0·57136
Titanium by difference.....	0·20264

These numbers give for the equivalent of titanium 314·37.

III. Chloride of titanium employed..	0·7775
Silver.....	1·74613
indicating Chlorine .....	0·57367
Titanium by difference.....	0·20383

The equivalent of titanium deduced from this experiment is 314·94.

IV.	Chloride of titanium employed..	0·716
	Silver.....	1·61219
indicating	Chlorine.....	0·52966
	Titanium by difference.....	0·18634
Equivalent of titanium 311·84.		
V.	Chloride of titanium employed..	0·8085
	Silver.....	1·82344
indicating	Chlorine.....	0·59907
	Titanium by difference.....	0·20943
Equivalent of titanium 309·38.		

The three first numbers agree perfectly, but the two latter are notably less, especially the last, since it differs from the three first by five whole numbers, or more than  $1\frac{1}{2}$  per cent. It was difficult to attribute this difference entirely to deficient precision in the method used. It occurred to the author that it might be owing to the partial decomposition of the chloride of titanium, by the moisture of the air during manipulation, and this was soon found to be the case by direct experiment.

M. Pierre proposes to adopt, as the nearest approximation to truth, 314·69, the mean of the three first experiments, as the equivalent number for titanium.

This number is very different from 355 deduced from 6·536, the density of the vapour of the chloride of titanium observed by M. Dumas. Its density, calculated from 314·69, would be 6·614.—*Ann. de Ch. et de Phys.*, Juillet 1847.

ON A MODIFICATION OF THE APPARATUS OF VARRENTTRAPP AND WILL FOR THE ESTIMATION OF NITROGEN. BY WARREN DE LA RUE.

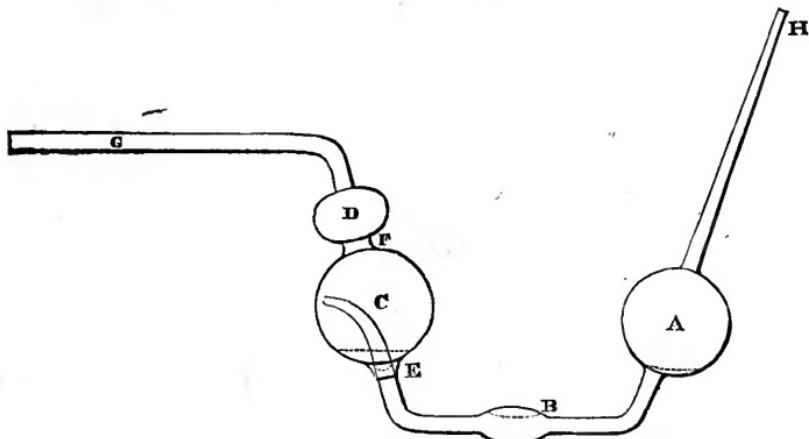
My attention having been called to a communication by Mr. Alex. Kemp in the number of the 'Chemical Gazette' for the 1st of April 1847, in which he describes a modification of Messrs. Varrentrapp and Will's tube for nitrogen determinations, of a very similar construction to one I employed as far back as November 1845 in the laboratory of the Royal College of Chemistry, and which I have repeatedly shown to my friends, I am induced to lay before the Society a description of my form of apparatus, which differs somewhat from that described by Mr. Kemp.

By the drawing, it will be seen that the tube B E, instead of opening immediately into the bottom of the flattened bulb C, is prolonged and rises for some distance into the bulb curving over towards its side; in this respect Mr. Kemp's apparatus does not differ materially from mine. I found it necessary however to have a third bulb (D) blown (which is best of a spheroidal form), in order to effectually prevent the acid from being drawn into the tube G whenever a sudden absorption took place; this third bulb communicates with C by a narrow neck. If the apparatus be constructed without

the third bulb D, a portion of fluid generally passes into the tube G from the rotary motion induced in the fluid in C.

The dotted lines indicate the height of fluid in the bulbs, and this quantity is quite sufficient for the condensation of all the ammonia likely to be formed. I would remark, that if during the progress of the combustion a cessation of the production of gas should occur, the construction of the apparatus is such as to prevent the whole of the acid ever being carried over into the bulb C, so that on the evolution again commencing no fear need be entertained for the complete condensation of the ammonia.

It only remains for me to add, that though this new form of apparatus is not so readily rinsed out as the original one of Messrs. Varrentrapp and Will, no great inconvenience is experienced from that cause, as the acid can, at the close of the operation, be easily caused to flow into the bulb C and out at the tube G, by properly inclining the bulbs, &c., and when this is done water or alcohol may be introduced by a pipette through the limb H.



*From the Proceedings of the Chemical Society.*

#### ON THE DETECTION OF COTTON IN LINEN. BY G. C. KINDT.

This subject has frequently engaged the attention of commercial and scientific men; many experiments have been made in order to detect cotton thread in linen; many processes have been recommended, but none have hitherto proved satisfactory. I was therefore much surprised when a stranger, a few weeks ago, showed me a sample of linen from the one-half of which all the cotton filaments had been eaten away. He had obtained it in Hamburg, and asked me whether I could give him a process for effecting this purpose. Now since, as far as I am aware, nothing has been published on this subject, and it is of very general interest, I consider it a duty to communicate the results of my experiments. I had already observed, in experimenting with explosive cotton, flax, &c., that these two substances behave somewhat differently towards concentrated acids; and although it has long been known that strong sulphuric acid con-

verts all vegetable fibre into gum, and when the action is continued for a longer period, into sugar, I found that cotton was metamorphosed much more rapidly by the sulphuric acid than flax. It is therefore by means of *concentrated sulphuric acid* that cotton may be removed from linen when mixed with it; and this object may be obtained by the following process:—

The sample to be examined must be freed as perfectly as possible from all dressing by repeated washing with hot rain- or river-water, boiling for some length of time, and subsequent rinsing in the same water; and I may expressly observe, that its entire removal is requisite for the experiment to succeed. When it has been well-dried, the sample is dipped for about half its length into common oil of vitriol, and kept there for about half a minute to two minutes, according to the strength of the tissue. The immersed portion is seen to become transparent. It is now placed in water, which dissolves out the gummy mass produced from the cotton; this solution may be expedited by a gentle rubbing with the fingers; but since it is not easy to remove the whole of the acid by repeated washing in fresh water, it is advisable to immerse the sample for a few instants in spirits of hartshorn (purified potash or soda have just the same effect), and then to wash it again with water. After it has been freed from the greater portion of the moisture by gentle pressure between blotting-paper, it is dried. If it contained cotton, the cotton threads are found to be wanting in that portion which had been immersed in the acid; and by counting the threads of the two portions of the sample, its quantity may be very readily estimated.

If the sample has been allowed to remain too long in sulphuric acid, the linen threads likewise become brittle, or even eaten away; if it were not left a sufficient time in it, only a portion of the cotton threads have been removed; to make this sample useful, it must be washed, dried, and the immersion in the acid repeated. When the tissue under examination consists of pure linen, the portion immersed in the acid likewise becomes transparent, but more slowly and in a uniform manner, whereas in the mixed textures the cotton threads are already perfectly transparent, while the linen threads still continue white and opaque. The sulphuric acid acts upon the flax threads of pure linen, and the sample is even somewhat transparent after drying as far as the acid acted upon it, but all the threads in the sample can be seen in their whole course.

Cotton stuffs containing no linen dissolve quickly and entirely in the acid; or if left but one instant in it, become so brittle and gummy that no one will fail to recognise it as cotton when treated in the above manner.—*Liebig's Annalen*, Feb. 1847.

#### THE PLANET HEBE\*.

On July 1, M. Henke of Driessen in Prussia, discovered another planet, which appears to belong to the singular group lying between the orbits of Mars and Jupiter. It was first observed accurately at

\* Communicated by J. R. Hind, Esq., F.R.A.S.

Berlin by Prof. Encke on July 5, and since that date observations have been made very generally at the different European observatories. The following are the elements according to different calculators:—

	Galle and d' Arrest.	Neumann.	Hind.
Epoch.	July 10°0 Berlin.	July 5°41864 Berlin.	July 0°0 Greenwich.
Mean anomaly .....	268° 55' 50"·5	283° 9' 44"·6	283° 56' 54"·0
Long perihelion'.....	19 4 14·9	9 3 9·6	8 17 24·1
Ascending node .....	139 5 3·1	138 12 16·2	137 25 35·1
Inclination .....	14 38 58·5	14 49 53·6	15 2 56·1
Sin⁻¹ e .....	10 41 16·7	13 5 48·2	13 49 20·0
Log. semi-axis major	0·3772450	0·3955266	0·4016899

The longitudes in first and second set are counted from M. Equinox of 1847·0; in the third set from M. Equinox of July 0.

#### METEOROLOGICAL OBSERVATIONS FOR JUNE 1847.

*Chiswick*.—June 1—3. Clear and very fine. 4. Light clouds and fine. 5. Cloudy. 6. Light clouds: clear. 7. Clear: cloudy. 8. Rain: thunder-showers. 9. Clear and fine. 10. Rain: cloudy: clear. 11, 12. Clear and very fine. 18. Rain: cloudy. 14. Densely clouded: showery. 15. Rain: thunder and heavy showers. 16. Cloudy: rain. 17, 18. Rain. 19. Cloudy and fine. 20. Cloudy: slight showers. 21. Cloudy: fine. 22. Very fine. 23. Very fine: heavy showers, with thunder. 24. Cloudy and fine. 25. Rain: cloudy and fine. 26. Very fine. 27. Drizzly: cloudy and fine. 28. Fine. 29. Very fine. 30. Light clouds: very fine: overcast.

Mean temperature of the month ..... 58°·46

Mean temperature of June 1846 ..... 66°·63

Mean temperature of June for the last twenty years ..... 66°·90

Average amount of rain in June ..... 1·88 inch,

*Boston*.—June 1—4. Fine. 5, 6. Cloudy. 7. Fine. 8. Fine: rain early A.M. 9. Fine. 10. Cloudy: rain early A.M.: showery all day. 11, 12. Fine. 18. Cloudy: rain early A.M. 14. Cloudy: rain early A.M.: rain P.M. 15. Fine: rain P.M. 16. Fine: rain A.M. and P.M. 17. Fine. 18. Cloudy: rain early A.M.: heavy rain P.M. 19. Cloudy: rain early A.M. 20. Cloudy: rain A.M. and P.M. 21. Cloudy: rain P.M. 22, 23. Fine: rain P.M. 24. Rain: rain P.M. 25. Fine: rain P.M. 26. Fine. 27. Cloudy. 28. Fine. 29, 30. Cloudy.—This month has been the coldest since 1843, and the wettest since June 1841.

*Sandwick Manse, Orkney*.—June 1, 2. Clear: fine. 3. Cloudy: fog. 4. Bright: cloudy. 5. Showers: cloudy. 6. Bright: cloudy. 7. Showers. 8. Bright: drops. 9. Cloudy: rain. 10. Showers: sleet-showers. 11. Bright: cloudy. 12. Cloudy. 13. Cloudy: rain. 14. Rain: damp. 15. Cloudy: rain: cloudy. 16. Cloudy: fine. 17, 18. Bright: fine. 19. Clear: fine. 20. Bright: rain. 21. Showers: clear. 22. Bright: showers: fine. 23. Bright: showers. 24. Bright: thunder: drops. 25. Bright: thunder. 26. Clear: fine. 27. Damp. 28. Cloudy. 29. Fog: cloudy. 30. Damp: fog.

*Applegarth Manse, Dumfries-shire*.—June 1—3. Very fine. 4. Warm, but overcast. 5. Fair A.M.: showers P.M. 6. Fair A.M. 7. Threatening: rain P.M. 8. Slight shower. 9. Fair: thunder: rain. 10. Fair: clear. 11. Fair, but cool. 12. Cloudy: rain P.M. 13. Rain. 14. Fine: thunder: rain. 15. Drizzly: thunder. 16. Bright A.M.: rain. 17. Drizzly. 18. Fair and fine. 19. Fine: a few drops. 20. Rain P.M. 21. Wet A.M.: cleared. 22. Showery. 23. Fine, very: slight shower. 24. Showery: thunder. 25. Showers A.M.: thunder. 26. Slight shower P.M. 27. Shower A.M.: fair. 28—30. Very fine.

Mean temperature of the month ..... 55°·2

Mean temperature of June 1846 ..... 63°·2

Mean temperature of June for 25 years ..... 56°·10

Mean rain in June for 20 years... ..... 2·32 inches.

*Meteorological Observations made by Mr. Thompson at the Garden of the Horticultural Society at Chiswick, near London; by Mr. Veall, at Boston; by the Rev. W. Dunbar, at Applegarth Manse, DUMFRIES-SHIRE; and by the Rev. C. Clouston, at Sandwick Manse, ORKNEY.*

THE  
LONDON, EDINBURGH AND DUBLIN  
**PHILOSOPHICAL MAGAZINE**  
AND  
**JOURNAL OF SCIENCE.**

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[THIRD SERIES.]

SEPTEMBER 1847.

XXIX. *On certain Products of Decomposition of the Fixed Oils in contact with Sulphur.* By THOMAS ANDERSON, Esq., M.D., F.R.S.E., *Lecturer on Chemistry, Edinburgh*.\*

NUMEROUS researches have established as a general rule that the products of the decomposition of organic substances vary with the circumstances of the experiment, and the nature of the agents under the influence of which it is performed. If, for instance, we examine the action of heat alone, we find it causing a set of decompositions specially characterized by the evolution of carbonic acid, formed by the union of part of the carbon of the substance with the whole or part of its oxygen; and this action is rendered more definite, and the number of the products circumscribed by all circumstances facilitating the formation of carbonic acid, such as the presence of a base, which will even cause its evolution when heat alone is incapable of producing decomposition. Acids, on the other hand, have a precisely opposite effect; they, in some instances, altogether prevent the formation of carbonic acid, and cause the oxygen to exert its action on the hydrogen of the compound, and to eliminate one or more atoms of water which do not generally exist ready formed in it.

In these particular instances, decomposition takes place at the expense of the constituent atoms of the compounds themselves, the extraneous substances serving merely as disponsants to the oxidation; in the one case of part of their carbon, in the other of their hydrogen. But there is another class of agents, which, besides eliminating one or more substances, are capable at the same time of entering into union with the residual atoms, and forming a new derivative of the original compound. The best investigated of this class of agents are chlo-

\* Read before the Royal Society of Edinburgh on the 19th of April, 1847, and published in their Transactions, vol. xvi. part 3, p. 363.

rine, bromine, nitric acid and ammonia ; the three former of which exert their action on the hydrogen, the latter on the oxygen of the substance, and form compounds, the complete investigation of which is important, not merely in a purely chemical point of view, but also from the light which they seem likely to throw on the general question of the atomistic constitution of matter. In fact, the great object of the researches of organic chemistry at the present moment is that of developing the relations which the individual atoms bear to the molecules of their compound, by a knowledge of which we hope eventually to arrive at some definite conclusions with regard to the mode in which the elementary atoms are grouped together in a complex molecule. Almost all the scanty information which we possess on this subject has been derived from investigating the products of the action of different agents upon organic substances ; and it is sufficiently obvious, that the more varied the circumstances, and numerous the points of view under which these reactions can be examined, so much the more likely are we to arrive at definite results.

It was the consideration of these points which led me to undertake an investigation into the nature of the action of sulphur in the free state upon organic compounds, a subject hitherto totally uninvestigated, unless we except the curious researches of Zeise\* on the simultaneous action of ammonia and sulphur upon acetone, which yields a variety of remarkable products, the properties of which he has described, without however determining their constitution. The results at which I have already arrived in these researches are contained in the following pages. They are, however, to be considered only as the commencement of the investigation ; and I am desirous of submitting them to the Society even in their present very imperfect state, as it is impossible to fix a period within which a series of researches, surrounded by so many difficulties, can be completed. No one who has not been specially occupied with such experiments can have any conception of the numerous sources of annoyance which they present, and of the expenditure of time and labour which is necessary for their performance. Indeed, I have more than once felt inclined altogether to abandon a subject occupying so much time in proportion to the results obtained, and the completion of which is further protracted by the nauseous odour of the compounds, which is so disgusting that it is impossible to pursue the investigation for any length of time continuously.

At the commencement of these researches I endeavoured to examine the action of sulphur upon some of the simpler

\* *Forhandlingar vid de Skandinaviska Naturforskarnes tredje möte*, p. 303.

organic compounds, in the hope of arriving at results of corresponding simplicity. My expectations, however, were disappointed, and I was obliged to have recourse to the fixed oils, on which sulphur has been long known to exert an action; the product obtained by heating together olive oil and sulphur until a uniform balsam-like substance was formed, having been employed in medicine by the older physicians under the name of the balsam of sulphur.

The phænomena which manifest themselves during the mutual action of sulphur and a fixed oil are these:—At the first application of heat, the sulphur melts and forms a stratum at the bottom of the oil; but as the temperature rises it slowly dissolves, with the formation of a thick viscid fluid of a dark red colour. As the heat approaches that at which the oil undergoes decomposition when heated alone, a violent action takes place attended by the evolution of sulphuretted hydrogen in such abundance, that the viscid mass swells up and occupies a space many times its original bulk. If at this point the mixture be allowed to cool, it concretes into a tough sticky tenacious mass, adhering strongly to the fingers, and having a disagreeable sulphureous odour; if however the heat be sustained, the frothing and evolution of sulphuretted hydrogen continue, and at the same time an oil of a peculiar disgusting odour, resembling that of garlic, but more disagreeable, passes into the receiver.

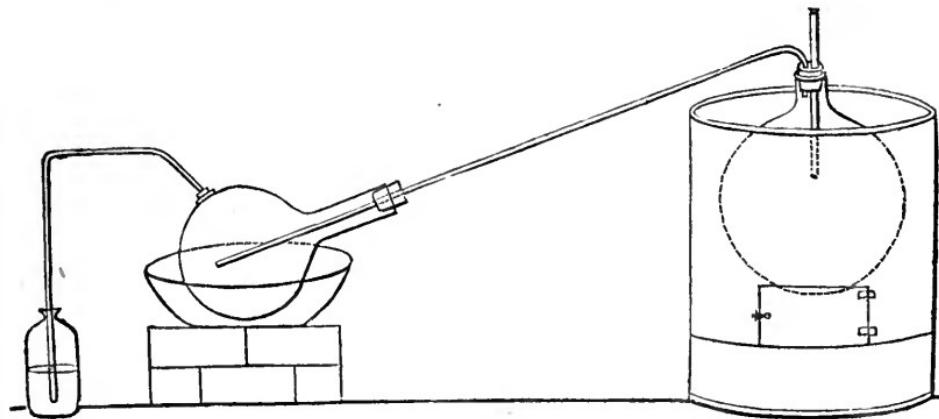
In the investigation of the products of this action, the first and most essential step was to determine the particular constituents of the oil from which they are derived. In order to do this, it was necessary to examine separately the action of sulphur upon each of its components. I commenced therefore by making use of stearic acid, which can be readily obtained in a pure state: experiment however showed that none of the peculiar products were derived from it; for when mixed with half its weight of sulphur and distilled, mere traces of sulphuretted hydrogen were evolved, and the products were identical with those obtained from the unmixed acid. The nauseous smelling oils being then obviously derived either from the oleic acid, or the glycerine of the oil, I prepared a quantity of pure oleic acid, by the decomposition of the æthereal solution of the oleate of lead. This, when mixed with half its weight of sulphur, and distilled in a capacious retort, underwent decomposition precisely as the crude fixed oil did; sulphuretted hydrogen was developed in great abundance, and the product of the distillation could not be distinguished from that which I had previously obtained. I was unable to obtain glycerine in sufficient quantity to make a separate investiga-

tion of the products of its decomposition ; but these must also be peculiar, as I could not distinguish the presence of acroleine during any period of the distillation of an oil with sulphur.

The product of the distillation of oleic acid was in the form of a reddish-brown oil, having an extremely nauseous odour, in which that of sulphuretted hydrogen was apparent. When rectified, this sulphuretted hydrogen was driven off, and the first portions which distilled were perfectly transparent and colourless. As the process continued, however, the products became gradually darker in colour, and the last portions which distilled became semisolid on standing, from the deposition of a quantity of white crystalline plates. These were separated by filtration through cloth, expressed strongly, and purified by successive crystallizations from alcohol, until they were entirely free from smell and colour. The product was then in the form of white pearly scales, which possessed acid properties, and were totally insoluble in water ; they were not therefore sebacic acid, no trace of which could be discovered among the products, but, on the contrary, possessed all the properties of margaric acid. These crystals were obtained from quantities of oleic acid, prepared at different times, and with the greatest possible care, and must have been formed during the decomposition. In order however to set this point at rest, some of the same oleic acid was distilled alone, when abundance of sebacic acid was obtained, and the latter portions of the rectified product did not deposit any crystals on cooling, but remained perfectly fluid. As this solid acid is produced only in comparatively small quantity, and I was unable to obtain enough of oleic acid, I made use, in preparing it on the large scale, of pure almond oil, which, according to Schübler and Gasserow, is entirely free of margarine. The oil which I employed was expressed specially for these experiments, at a temperature slightly above  $32^{\circ}$  ; and in order to satisfy myself of the absence of margaric acid in the products of its ordinary decomposition, a quantity was distilled alone, and the product rectified. The latter portions being collected apart did not deposit margaric acid ; and this I have also found to be the case with the ordinary almond oil of commerce, in the expression of which a moderate degree of heat is employed.

In distilling the oil and sulphur on the large scale, it became impossible to perform the process by the simple admixture of the substances, the frothing being so great as inevitably to expel the materials from the retort. After a trial of various methods, I found it most convenient to employ the apparatus, of which this is a sketch. The oil was introduced into a large

glass balloon, to the mouth of which two tubes were adapted, one descending to near the middle, and furnished with a cork



at the upper end, the other which constituted the neck of the distilling apparatus passed into a tubulated receiver, kept cold by immersion in water or ice. To the tubulation, a doubly bent tube was affixed, which descended into a vessel of alcohol, for the purpose of retaining any of the more volatile portions which might be carried over by the rapid current of sulphuretted hydrogen. The heat must be applied by means of an open charcoal fire; and the furnace should be so constructed that the fire may be rapidly withdrawn in the event of the action becoming too violent. It is very desirable too that the balloon should go down into the furnace, so that it may be entirely surrounded by hot air. The oil is introduced into the balloon, of which it must not occupy more than a fifth, or a fourth at most, along with a few small pieces of sulphur, and heat is gradually applied. So soon as effervescence commences, the cork of the small tube is withdrawn, and a small piece of sulphur is introduced; and this is continued gradually, so as to keep up a uniform action. A dark reddish-brown oil passes into the receiver, and at the same time sulphuretted hydrogen passes in torrents through the alcohol; it there deposits a certain quantity of oil, and on escaping, may be kept burning during the whole operation, with a flame eight or nine inches high. The principal difficulty of this process consists in regulating the heat, so as to keep up a steady action. If the heat be allowed to fall, the contents of the balloon become so viscid as inevitably to boil over; and at the same time too high a temperature causes the whole action to go on with

excessive violence. I have generally operated on quantities of three pounds, each of which requires a complete day for its distillation, during which time the operator must never leave it, but constantly attend to the regulation of the heat, and the gradual addition of sulphur in small quantities. When a quantity equal to about half the oil employed has distilled over, the remaining mass becomes excessively viscid; and just at this point the balloon frequently cracks, the contents escape, and the whole catches fire, and blazes off with a bright yellow flame and smell of sulphurous acid.

The product of this distillation, which exactly resembled that of the pure oleic acid, was rectified, and the crystals which deposited from the latter portions were expressed and purified by successive crystallizations in alcohol. They then presented all the characters of margaric acid, and gave the following results of analysis:—

I.	$\left\{ \begin{array}{l} 5.275 \text{ grains of the acid gave} \\ 14.558 \dots \text{ carbonic acid, and} \\ 5.919 \dots \text{ water.} \end{array} \right.$
II.	$\left\{ \begin{array}{l} 6.358 \text{ grains of the acid gave} \\ 17.578 \dots \text{ carbonic acid, and} \\ 7.212 \dots \text{ water.} \end{array} \right.$

Which gives the following results per cent.:—

	Experiment.		Calculation.	
	I.	II.	C <sub>34</sub>	H <sub>34</sub>
Carbon .	75.27	75.40	75.55	C <sub>34</sub> 2500.0
Hydrogen .	12.51	12.66	12.59	H <sub>34</sub> 425.0
Oxygen .	12.22	11.94	11.86	O <sub>4</sub> 400.0
	100.00	100.00	100.00	3325.0

These results agree completely with the formula for margaric acid, and were further confirmed by the analysis of its silver salt and æther.

4.643 grains of the silver salt gave 1.325 of silver = 28.53 per cent.

7.926 grains of the silver salt gave 2.284 of silver = 28.70 per cent.

The calculated result for margarate of silver gives 28.65 per cent.

The æther was prepared in the usual manner, by dissolving the acid in absolute alcohol, and passing dry hydrochloric acid gas through the solution. The product, which possessed all the properties of margaric æther, gave the following results of analysis:—

$\left\{ \begin{array}{ll} 5.596 \text{ grains of the aether gave} \\ 15.662 \dots \text{ carbonic acid,} \\ 6.399 \dots \text{ water.} \end{array} \right.$

	Experiment.	Calculation.		
Carbon . . .	76.33	76.51	$C_{38}$	2850.0
Hydrogen . . .	12.70	12.74	$H_{38}$	475.0
Oxygen . . .	10.97	10.79	$O_4$	400.0
	100.00	100.00		3725.0

These analyses establish, in a satisfactory manner, that the acid produced was margaric acid. It is scarcely possible however, in the present state of the investigation, to give anything like a rational explanation of the mode in which it is here formed. Its production from oleic acid has been already observed by Laurent as the first product of oxidation by nitric acid; but the action of sulphur is certainly of a very different character, and cannot be considered as bearing any analogy to that of an oxidizing agent. The quantity of margaric acid produced does not appear to be constant, but varies with the rapidity of the distillation, and is always most abundant when it is slowly performed.

The oil which distils previous to and along with the margaric acid, and constitutes by far the most abundant product of the action of sulphur upon oleic acid and oil of almonds, is a very complex substance, and contains some of its constituents in very small proportion. On this account I found it necessary to prepare it in very large quantity; and in doing so I abandoned the use of almond oil and employed linseed oil instead, which is a much cheaper substance, and yields the same fluid products. When the product of the action of sulphur is carefully rectified, the first portions which pass over are perfectly transparent and colourless, highly limpid and mobile, and boil at the temperature of  $160^{\circ}$  Fahr. Only a small quantity however passes at this temperature, and the immersed thermometer gradually rises without indicating any fixed boiling-point for the fluid. My first attempts to purify this oil and separate it into its various constituents, did not afford any satisfactory conclusions. Numerous analyses of the more volatile portions were made without obtaining comparable results, although all indicated the presence of carbon and hydrogen nearly in the proportion of equal atoms. The following are the details of three of these analyses:—

I.  $\left\{ \begin{array}{ll} 4.657 \text{ grains of the most volatile oil gave} \\ 12.688 \dots \text{ carbonic acid, and} \\ 5.127 \dots \text{ water.} \end{array} \right.$

- II.  $\left\{ \begin{array}{l} 5\cdot501 \text{ grs. of an oil less volatile than the preceding gave} \\ 15\cdot762 \dots \text{ carbonic acid, and} \\ 6\cdot292 \dots \text{ water.} \end{array} \right.$
- III.  $\left\{ \begin{array}{l} 4\cdot191 \text{ grains of another portion of oil gave} \\ 12\cdot185 \dots \text{ carbonic acid, and} \\ 4\cdot720 \dots \text{ water.} \end{array} \right.$

Which correspond to the following results per cent. :—

	I.	II.	III.
Carbon . .	75·03	78·79	79·95
Hydrogen .	12·20	12·72	12·75

All these oils, when treated with fuming nitric acid, yielded an abundant precipitate of the sulphate of barytes; but as the results of the combustion were not constant, no quantitative determination was made.

The action of precipitants however upon this oil afforded a more satisfactory method of obtaining some of its constituents. It gives with corrosive sublimate a bulky white precipitate, and with bichloride of platinum a yellow compound, the characters of which vary slightly, according as it is prepared from the more or less volatile portion of the oil. Nitrate of silver and acetate of lead, mixed with the alcoholic solution of the oil, produce only a slight cloudiness, but on boiling the solutions, the sulphurets of silver and lead are deposited.

*The Mercury Compound.*—In order to obtain this substance in the pure state, the oil was dissolved in alcohol, and an alcoholic solution of corrosive sublimate added. The precipitate which fell was collected on a filter, and washed with æther until the oil was thoroughly extracted, for which purpose a considerable quantity of æther is required. It is then boiled with a large quantity of alcohol, which dissolves a part of it; and the solution being filtered hot, allows the compound to deposit, on cooling, in the pure state. It is then in the form of a white crystalline powder, having a very fine pearly lustre, and exhibiting under the microscope crystals of a very peculiar form. They are six-sided tables, two opposite angles of which are rounded off, so as to give them a very close resemblance to the section of a barrel. It possesses, even after long-continued washing with æther, a peculiar slight sickening smell, which becomes more powerful on heating, and its powder irritates the nose. It is insoluble in water, which moistens it with difficulty. It requires several hundred times its weight of boiling alcohol for solution, and is almost entirely deposited, on cooling, in microscopic crystals. In æther it is almost insoluble. When heated, it is decomposed with the evolution

of a peculiar nauseous smelling oil. The sparing solubility of this compound in alcohol renders its preparation in sufficient quantity for analysis an extremely tedious process, and I have sought in vain for a more abundant solvent. The only substance which I have found capable of taking it up in larger quantity is coal-tar naphtha; but its employment is inadmissible, as the best which can be procured is an extremely impure substance, and the crystals of the compound deposited from it always acquire a rose or violet tint from some of its impurities. Oil of turpentine likewise dissolves it, but not more abundantly than alcohol.

By many successive solutions in alcohol, I obtained enough of this substance for an analysis, of which the following are the results :—

$\left\{ \begin{array}{ll} 12.302 \text{ grains, dried } in \text{ vacuo, gave} \\ 6.592 \dots \text{ of carbonic acid, and} \\ 3.018 \dots \text{ of water.} \end{array} \right.$

8.061 grains deflagrated with a mixture of nitre and carbonate of soda, gave 7.297 grains of sulphate of baryta = 1.0067 = 12.48 per cent. of sulphur.

The mercury and chlorine were determined together by mixing the substance with quicklime, and introducing the mixture into a combustion-tube. The end was then drawn out into an elongated bulb, into which the mercury sublimed, and which was afterwards cut off, dried in the water-bath, and weighed, both with and without the mercury; the chlorine was determined in the usual way from the residue in the tube.

9.958 grains gave 5.976 mercury = 60.01 per cent., and 4.310 grains chloride of silver = 10.67 per cent. of chlorine.

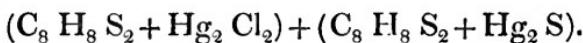
5.797 grains gave 2.409 of chloride of silver = 10.25 per cent. of chlorine.

These results correspond closely with the formula  $C_{16}H_{16}S_5Hg_4Cl_2$ , as is shown by the following comparisons :—

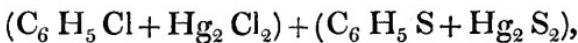
	Experiment.		Calculation.		
	I.	II.			
Carbon .	14.61	...	14.46	$C_{16}$	1200.0
Hydrogen .	2.72	...	2.42	$H_{16}$	200.0
Mercury .	60.01	...	60.32	$Hg_4$	5003.6
Chlorine .	10.67	10.25	10.67	$Cl_2$	885.3
Sulphur .	12.48	...	12.13	$S_5$	1005.8
	100.49		100.00		8294.7

It is sufficiently obvious that the formula  $C_{16}H_{16}S_5Hg_4Cl_2$

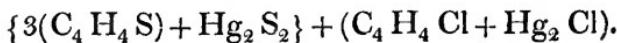
cannot be supposed to represent the rational formula of this substance. On the contrary, the remarkable analogy between its properties and those of the mercury compound of sulphuret of allyle appear clearly to indicate a similarity in their chemical constitution,—a similarity which, as we shall afterwards see, is borne out by the properties of the platinum compound. I consider this substance to contain an organic sulphuret analogous to sulphuret of allyle, the constitution of which must be represented by the formula  $C_8 H_8 S_2$ , to which I give the provisional name of sulphuret of odmyle (from  $\delta\delta\mu\eta$ , *odour*), and that the rational formula of the mercury compound is—



On contrasting this with the formula of the allyle compound, which is—



two important points of difference are apparent, namely, that in the new compound we have the sulphuret, and not the chloride, of the base in union with corrosive sublimate, and the presence of subsulphuret in place of sulphuret of mercury in the second member of the compound. It is even possible to approximate more closely the formulæ of the allyle and odmyle compounds, by assuming the sulphuret of odmyle to be represented by  $C_4 H_4 S$ ; in which case the mercury compound becomes—



This formula is however incompatible with its reactions, as it involves the presence of calomel in the compound. Treatment with caustic potash however shows that this is not the case, as it immediately becomes yellow, from the separation of oxide of mercury, while the black suboxide would have been formed had calomel been present.

When a current of sulphuretted hydrogen is passed through the mercury compound suspended in water, it becomes rapidly black, a peculiar smell is observed, along with that of sulphuretted hydrogen; and by distillation an oil passes over, which is obtained floating on the surface of the water. It is perfectly transparent and colourless. Its smell is peculiar, and resembles the nauseous odour developed by crushing some umbelliferous plants. When dissolved in alcohol, it gives with corrosive sublimate a white precipitate, soluble in hot alcohol, from which it is deposited in crystals precisely similar to those from which it had been originally separated, and with bichloride of platinum a yellow precipitate, slightly soluble in

hot alcohol and æther. This oil is in all probability the sulphuret of odmyle  $C_8 H_8 S_2$ ; but the small quantity in which I have been able to obtain it, has prevented my performing any analysis of it.

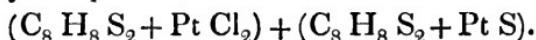
*The Platinum Compound.*—When a solution of bichloride of platinum is added to the alcoholic solution of the crude oil, a yellow precipitate makes its appearance, which does not fall immediately, but goes on gradually increasing for some time, precisely as is the case with the allyle compound. The properties of this precipitate are not however perfectly constant, but vary according to the portion of the oil employed to yield it. That obtained from the more volatile portion has a fine sulphur-yellow colour, but the less volatile oil gives an orange precipitate. It is insoluble in water, sparingly soluble in alcohol and æther. When heated it becomes black, an oil is evolved smelling exactly like that obtained from the mercury compound, and sulphuret of platinum is left behind, which requires a high temperature to drive off all its sulphur, and leaves metallic platinum as a silver-white mass. When treated with hydrosulphuret of ammonia, it is converted into a brown powder, exactly like that obtained under similar circumstances from allyle.

The analysis of the yellow compound has not hitherto given results of a satisfactory character. I have found the amount of platinum to oscillate between 43·06 and 49·66 per cent. The former of these was obtained from the most volatile oil, the latter from that which boiled between 300° and 400° F., and intermediate results were obtained at intermediate temperatures. The results obtained from the oil which boiled at a high temperature were remarkably constant; thus I have found, in different experiments, 49·00, 49·51, and 49·66 per cent. of platinum, which appear to indicate the presence of some compound of rather sparing volatility. The precipitate obtained from the most volatile oil appears to be that corresponding to the mercury compound which has just been described. Of it I have been able only to perform a very incomplete analysis, which is insufficient to establish its constitution, especially as it is impossible to ascertain whether it is a homogeneous substance. As the results, however, approximate to a formula analogous to that of the mercury compound, I give the details, such as they are.

$\left\{ \begin{array}{l} 9\cdot155 \text{ grains of the platinum compound gave} \\ 7\cdot474 \quad \dots \quad \text{carbonic acid, and} \\ 3\cdot294 \quad \dots \quad \text{water.} \end{array} \right.$

5·701 grains gave 2·455 grains of platinum = 43·06 per cent.

These results approximate to a formula similar to that of the mercury compound; viz.—



	Experiment.	Calculation.	
Carbon . . .	22.26	20.83	C <sub>16</sub> 1200.0
Hydrogen . . .	3.99	3.47	H <sub>16</sub> 200.0
Platinum . . .	43.06	42.84	Pt <sub>2</sub> 2466.6
Chlorine . . .	...	15.38	Cl <sub>2</sub> 885.3
Sulphur . . .	...	17.48	S <sub>5</sub> 1005.8
		100.00	5757.7

The analogy which those substances bear to allyle is exceedingly interesting, as showing the possibility of forming, by artificial processes, substances similar in constitution to so remarkable a compound, which is not a product of decomposition, but exists ready-formed in a variety of different vegetables, where it must obviously be produced under circumstances very different from the artificial substance; for allyle cannot exist at all at a high temperature, and is entirely decomposed at, or even below, its point of ebullition. Unfortunately, however, the examination of this substance is much complicated by the necessity of examining its compounds in place of itself. Had it been possible to separate it directly from the crude oil, the determination of its constitution and that of its compounds would have presented comparatively little difficulty, and been arrived at with much less labour than that expended upon the imperfect details I have been able to accumulate. Another point worthy of observation, is the total alteration of the products of decomposition of oleic acid produced by the presence of sulphur; no sebacic acid, and, in fact, none of its ordinary products being evolved, although all the substances produced contain carbon and hydrogen in the proportion of equal atoms, just as they exist among the ordinary products,—a circumstance which, taking into consideration the abundant evolution of sulphuretted hydrogen, we certainly should not have anticipated.

The oil which remains after the separation of the mercury compound, likewise contains sulphur as one of its constituents; but I have not yet had time to commence the investigation of this part of the subject. The discussion of it, as well as various other points connected with the compounds already described, I hope to make the subject of a future communication.

**XXX. On the Mechanical Equivalent of Heat, as determined by the Heat evolved by the Friction of Fluids. By J. P. JOULE, Secretary to the Literary and Philosophical Society of Manchester\*.**

IN the Philosophical Magazine for September 1845 I gave a concise account of some experiments brought before the Cambridge Meeting of the British Association, by which I had proved that heat was generated by the friction of water produced by the motion of a horizontal paddle-wheel. These experiments, though abundantly sufficient to establish the equivalency of heat to mechanical power, were not adapted to determine the equivalent with very great numerical accuracy, owing to the apparatus having been situated in the open air, and having been in consequence liable to great cooling or heating effects from the atmosphere. I have now repeated the experiments under more favourable circumstances, and with a more exact apparatus, and have moreover employed sperm oil as well as water with equal success.

The brass paddle-wheel employed had, as described in my former paper, a brass framework attached, which presented sufficient resistance to the liquid to prevent the latter being whirled round. In this way the resistance presented by the liquid to the paddle was rendered very considerable, although no splashing was occasioned. The can employed was of copper, surrounded by a very thin casing of tin. It was covered with a tin lid, having a capacious hole in its centre for the axle of the paddle, and another for the insertion of a delicate thermometer. Motion was communicated to the paddle by means of a drum fitting to the axle, upon which a quantity of twine had been wound, so as by the intervention of delicate pulleys to raise two weights, each of 29 lbs., to the height of about  $5\frac{1}{4}$  feet. When the weights in moving the paddle had descended through that space, the drum was removed, the weights wound up again, and the operation repeated. After this had been done twenty times, the increase of the temperature of liquid was ascertained. In the second column of the following table the whole distance through which the weights descended during the several experiments is given in inches. I may observe also that both the experiments on the friction of water, and the interpolations made in order to ascertain the effect of the surrounding atmosphere, were conducted under similar circumstances, each occupying forty minutes.

\* Read before the Mathematical and Physical Section of the British Association at Oxford, and communicated by the Author.

TABLE I.—Friction of Distilled Water.

Nature of experiment.	Total descent of each weight of 29 lbs. in inches.	Mean temperature of the room.	Difference.	Temperature of the water.		Gain or loss of heat.
				Before experiment.	After experiment.	
Friction .....	1268·5	60°839	0°040—	60°452	61°145	0°693 gain.
Interpolation	0	61·282	0·120—	61·145	61·180	0·035 gain.
Friction .....	1266·1	61·007	0·408+	61·083	61·748	0·665 gain.
Interpolation	0	61·170	0·570+	61·752	61·729	0·023 loss.
Friction .....	1265·8	57·921	0·809—	56·752	57·472	0·720 gain.
Interpolation	0	58·119	0·628—	57·472	57·511	0·039 gain.
Friction .....	1265·4	58·152	0·293—	57·511	58·207	0·696 gain.
Interpolation	0	58·210	0·003+	58·207	58·219	0·012 gain.
Friction .....	1265·1	57·860	0·215+	57·735	58·416	0·681 gain.
Interpolation	0	58·162	0·256+	58·416	58·420	0·004 gain.
Friction .....	1265·3	57·163	0·220+	57·050	57·716	0·666 gain.
Interpolation	0	57·602	0·121+	57·716	57·731	0·015 gain.
Friction .....	1265·2	57·703	0·359+	57·731	58·393	0·662 gain.
Interpolation	0	58·091	0·304+	58·393	58·397	0·004 gain.
Friction .....	1262·4	56·256	0·015—	55·901	56·582	0·681 gain.
Interpolation	0	56·888	0·285—	56·590	56·617	0·027 gain.
Friction .....	1262·3	57·041	0·078—	56·617	57·310	0·693 gain.
Interpolation	0	57·612	0·285—	57·310	57·344	0·034 gain.
Mean friction experiments }	1265·13	.....	0·0037—	.....	.....	0·6841 gain.
Mean of the interpolations }	0	.....	0·0071—	.....	.....	0·0163 gain.
Corrected result .....	1265·13	.....	.....	.....	.....	0·6680 gain.

We see then that the weights of 29 lbs., in descending through the altitude of 1265·13 inches, generated 0°·668 in the apparatus. But in order to reduce these quantities, it became necessary in the first place to ascertain the friction of the pulleys and that of the twine in unwinding from the drum. This was effected by causing the twine to go once round a roller of the same diameter as the drum, working upon very fine pivots, the two extremities of the twine being thrown over the pulleys. Then it was found that, by adding a weight of 3150 grains to either of the two weights, the friction was just overcome. The actual force employed in the experiments would therefore be 406000 grs. — 3150 grs. = 402850 grs. through 1265·13 inches, or 6067·3 lbs. through a foot.

The weight of water being 77617 grs., that of the brass paddle-wheel 24800 grs., the copper of the can 11237 grs.,

and the tin casing and cover 19396 grs., the whole capacity of the vessel and its contents was estimated at  $77617 + 2319 + 1056 + 363 = 81355$  grs. of water. Therefore the quantity of heat evolved in the experiments, referred to a pound of water, was  $7^{\circ} \cdot 7636$ .

The equivalent of a degree of heat in a pound of water was therefore found to be 781·5 lbs. raised to the height of one foot.

I now made a series of experiments in which sperm oil was substituted for the water in the can. This liquid, being that employed by engineers as the best for diminishing the friction of their machinery, appeared to me well-calculated to afford another and even more decisive proof of the principles contended for.

TABLE II.—Friction of Sperm Oil.

Nature of experiment.	Total descent of each weight of 29 lbs. in inches.	Mean temperature of the room.	Difference.	Temperature of the oil.		Gain or loss of heat.
				Before experiment.	After experiment.	
Friction .....	1263·8	56·677	0·453+	56·354	57·906	1·552 gain.
Interpolation	0	57·316	0·595+	57·906	57·917	0·011 gain.
Friction .....	1269·0	56·198	1·024+	56·516	57·929	1·413 gain.
Interpolation	0	56·661	1·221+	57·929	57·836	0·093 loss.
Friction .....	1268·7	57·958	0·588+	57·813	59·280	1·467 gain.
Interpolation	0	57·051	0·773+	57·836	57·813	0·023 loss.
Friction .....	1268·5	58·543	1·685-	55·951	57·766	1·815 gain.
Interpolation	0	57·153	1·504-	55·568	55·731	0·163 gain.
Friction .....	1268·1	59·097	0·534-	57·766	59·361	1·595 gain.
Interpolation	0	57·768	1·927-	55·731	55·951	0·220 gain.
Friction .....	1268·3	56·987	0·186-	56·029	57·573	1·544 gain.
Interpolation	0	57·156	0·413+	57·573	57·565	0·008 loss.
Friction .....	1268·7	57·574	0·734+	57·581	59·036	1·455 gain.
Interpolation	0	57·336	0·237+	57·565	57·581	0·016 gain.
Friction .....	1267·6	58·537	0·829-	56·884	58·532	1·648 gain.
Interpolation	0	59·641	0·364+	60·026	59·984	0·042 loss.
Friction .....	1268·0	59·131	0·148+	58·532	60·026	1·494 gain.
Interpolation	0	60·164	0·138-	59·984	60·069	0·085 gain.
Mean friction experiments	1267·85	.....	0·034+	.....	.....	1·5537 gain.
Mean of the interpolations	0	.....	0·004+	.....	.....	0·0366 gain.
Corrected result .....	1267·85	.....	.....	.....	.....	1·5138 gain.

In this instance, the force employed, corrected as before for the friction of the pulleys, was equal to raise 6080·4 lbs. to the height of one foot.

In estimating the capacity for heat of the apparatus, it was necessary in this instance to obtain the specific heat of the sperm oil employed. For this purpose I employed the *method of mixtures*. 43750 grs. of water were heated in a copper vessel weighing 10403 grs. to 82°·697. I added to this 28597 grs. of oil at 55°·593, and after stirring the two liquids together, found the temperature of the mixture to be 76°·583. Having applied to these data the requisite corrections for the cooling of the liquids during the experiment, and for the capacity of the copper vessel, the specific heat of the sperm oil came out 0·45561. Another experiment of the same kind, but in which the water was poured into the heated oil, gave the specific heat 0·46116. The mean specific heat was therefore 0·45838.

The weight of oil employed was 70273 grains, and the paddle, can, &c. were the same as employed in the first series of experiments; consequently the entire capacity in this instance will be equivalent to that of 35951 grs. of water. The heat evolved was therefore 7°·7747 when reduced to the capacity of a pound of water.

Hence the equivalent deduced from the friction of sperm oil was 782·1, a result almost identical with that obtained from the friction of water. The mean of the two results is 781·8\*, which is the equivalent I shall adopt until further and still more accurate experiments shall have been made.

**XXXI. Letter from Prof. SCHÖENBEIN to Prof. FARADAY,  
F.R.S., on a new Test for Ozone†.**

MY DEAR FARADAY,

**H**AVING a good opportunity for sending you a few lines, I will make use of it to tell you something about my little doings. You are no doubt struck with the peculiarity of the ink in which this letter is written, and I am afraid you will think it a very bad production; but in spite of its queer colour, you will like it when I tell you what it is, and when I

\* This number is slightly different from 775, the equivalent stated at Oxford, and used by me as one of the data for calculations on the velocity of sound. The reason of the difference was that by an oversight I had taken the friction of *both* pulleys as the correction of each weight instead of both weights. The whole of the experiments are exactly the same as those presented to the Oxford meeting. The slight alteration in the equivalent will make only a very trifling alteration in the theoretical velocity of sound given in the last Number of this Magazine.

† Communicated by Professor Faraday.

assure you that as long as the art of writing has been practised no letter has ever been written with such an ink. Dealing now again in my ozone business, I found out the other day that all manganese salts, be they dissolved or solid, are decomposed by ozone, hydrate of peroxide of manganese being produced and the acid set at liberty. Now to come round again to my ink, I must tell you that these lines are written with a solution of sulphate of manganese. The writing being dry, the paper is suspended within a large bottle, the air of which is strongly ozonized by means of phosphorus. After a few minutes the writing becomes visible, and the longer you leave it exposed to the action of ozone the darker it will become. Sulphurous acid gas uniting readily with the peroxide of manganese to form a colourless sulphate, the writing will instantly disappear when placed within air containing some of that acid; and it is a matter of course that the writing will come out again when again exposed to ozonized air. Now all this is certainly mere playing; but the matter is interesting in a scientific point of view, inasmuch as dry strips of white filtering paper drenched with a weak solution of sulphate of manganese furnish us with rather a delicate and specific test for ozone, by means of which we may easily prove the identity of chemical, voltaic and electrical ozone, and establish with facility and certainty the continual presence of ozone in the open air. I have turned brown my test-paper within the electrical brush, the ozonized oxygen obtained from electrolysed water and the atmospheric air ozonized by phosphorus. The quantity of ozone produced by the electrical brush being so very small, it requires of course some time to turn the test-paper brown.

As it is rather inconvenient to write with an invisible ink, I will stop here; not however before having asked your kind indulgence for the many blunders and faults which my ozone bottle will no doubt bring to light before long.

Yours most truly,

C. F. SCHÖENBEIN.

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XXXII. *On the Decomposition of Water by Platinum and the Black Oxide of Iron at a white heat, with some observations on the theory of Mr. Grove's Experiments.* By GEORGE WILSON, M.D.\*

THE remarkable discovery recently made public by Mr. Grove, that water in certain circumstances, when raised to a white heat, is resolved into its constituent gases, has na-

\* Communicated by the Chemical Society; having been read March 15, 1847.

turally excited much attention. It furnished the unexpected confirmation of the truth of an opinion expressed by James Watt so far back as 1783, that if steam could be made red hot [white hot] so that all its latent heat should be converted into sensible heat, either the steam would be converted into permanent air, or some other change would take place in its constitution\*.

In the greater number of Mr. Grove's experiments, water was raised in temperature through the medium of platinum; and it became a question accordingly, as Sir John Herschel and my friend Dr. Lyon Playfair suggested, how far the decomposition of water observed was owing to the mere heat of the metal, how far to the peculiar surface-influence, or so-called catalytic force, which has been so long recognized as possessed by platinum and the other noble metals. Dr. Playfair also referred to the fact, "that many bodies at high temperatures exhibited a great affinity for oxygen, which they did not possess at lower temperatures; as, for instance, silver, gold, and even platinum itself, which metals absorb oxygen when intensely heated, and give it out again on cooling. If the experiments had been tried in tubes of quartz or silica, they would not have been open to the objection which the use of so peculiar a metal as platinum appeared to involve†."

There was indeed one form of Mr. Grove's experiment not liable to the exception urged against those where platinum was used. He found it quite possible to decompose steam by sending Leyden-jar discharges through it, and refers the decomposition solely to the heat evolved by the electric spark. The same view has been suggested as not improbable by Faraday, in relation to the decomposition of water in the liquid form by electric discharges ‡. With great diffidence, however, I would remark, that the spark decomposition of water cannot be regarded as an *experimentum crucis*. Although the electric spark cannot decompose steam electrolytically, we may not at once infer that it cannot decompose it in another way. I have no wish to assert that it can, but it is possible that it may, and a crucial experiment should be unexceptionable. Again: the spark discharge of a Leyden jar exerts a great disruptive force, and acts topically with much violence. There is reason moreover to believe that mechanical agitation or disturbance of a chemical compound can in many cases cause the separation of its elements. It may seem an extravagant idea to suppose that oxygen may be torn or detached from hydrogen by the action of a dis-

\* Phil. Trans. 1783, p. 416.

† Athenaeum for September 19th, 1846, p. 966.

‡ Researches in Electricity, 3rd series, paragraph 337.

ruptive force on the molecules of water, as if chemical affinity were but a kind of mechanical cohesion, which may be overcome by division. On the other hand, however, it must not be forgotten, that we are now acquainted with a large number of fulminating compounds, which can be decomposed by friction, by a touch, or a stroke. These compounds are all fragile, and water is a very stable combination; but fragility and stability are but terms of degree, in relation to stability of union: and if it shall appear that a feeble mechanical force can overcome a small intensity of affinity, it will be acknowledged as quite possible that a powerful mechanical agency may overcome a great one. We have no means perhaps of making an unexceptionable experiment as to the decomposing power of mechanical force; for we cannot bring it into play without calling into action other agencies. If we touch, or rub, or strike a fulminate, for example, we cause the evolution of heat, and add its decomposing power to that of the mechanical impulse. It would be a mere *petitio principii*, however, to assume that the heat produced alone effects the decomposition observed. It seems to me, therefore, that the decomposition of steam by the electric spark furnishes a more complex problem for solution than the action of white-hot platinum on the same compound does; and that the experiments made with the metal are more likely to throw light on those tried with the spark, than to be explained by them.

Whilst thinking over these difficulties, and the objections to Mr. Grove's conclusions suggested by Herschel and Playfair, I had occasion to perform the familiar class-experiment of burning iron wire in oxygen. I observed with an interest I had not felt previously, although I had carelessly noticed the phænomenon before, that bubbles of apparently permanent gas rose from the globules of white-hot oxide of iron as they fell into the water. It seemed to me possible that this gas might be a mixture of oxygen and hydrogen separated by the influence of the metallic oxide, acting as platinum did in Mr. Grove's experiments. It was certain, moreover, that if this should prove to be the case, it would supply a powerful argument in favour of that gentleman's conclusion, which seems, in spite of all the objections noticed, in the highest degree probable, namely, that heat, apart altogether from the medium through which it is applied, can resolve water into its elements.

As the following experiments were made solely in the hope of substantiating Mr. Grove's view, which unfortunately, however, they leave exactly as they found it, I trust that gentleman will not consider their publication an interference with his researches. I was led to try them incidentally, and

abandoned them as soon as I found I could render Mr. Grove no assistance by means of them.

It would be difficult to conceive a more rapid and effectual way of raising a body to a white heat than that afforded by the combustion of iron in oxygen. I took for granted also (as it afterwards appeared, too hastily) that the metal could not but be saturated with oxygen and converted into a definite oxide, which would be chemically indifferent to each of the elements of water, and if it decomposed it at all, would reject both its constituents. The convenient way, moreover, in which the globules of oxide detach themselves and fall into the water, and the rapidity with which the whole process goes on, make it a very easy matter to collect in considerable quantity whatever gases are evolved. A stoppered bottomless jar of the ordinary construction for the iron-wire experiment, and of 291 cubic inches' capacity, was made use of in the following trials. Eighteen experiments were made with it, and from 100 to 110 grains of fused globules were obtained from each combustion. A test-tube, with a funnel fixed into it by a perforated cork, and filled with water, was arranged so as to receive the gas. In some experiments it was placed within the oxygen jar, so that the coil of wire when introduced hung close to it, a piece of tin plate being arranged so as to guide the globules within the edge of the inverted funnel. In the greater number of trials however the tube and funnel were placed outside of the vessel containing the oxygen, and an inclined plane of tin plate was so placed as to carry the globules past the edge of the jar, and within the mouth of the funnel. No difference of result was observed in experiments made in both ways, but the latter arrangement was preferred as more convenient, and as enabling more oxygen to be employed at each trial.

In all the experiments, permanent gas was evolved when the fused globules fell into the water. This statement is to be considered as applying to each combustion considered as a whole; for individual globules were frequently observed to give off no gas at all, or to evolve so very little, that it might be air separating from the water, in which it had previously existed in solution. The quantity of gas obtained at each combustion varied greatly. Sometimes as much as a cubic inch was procured, more frequently only half that quantity, and occasionally less. The globules from thick coils of wire gave off a larger volume of gas than those from thin ones.

Portions of the gas were transferred to a Grove's audiometer over water, and exposed to a white-hot platinum wire. They did not kindle or detonate, nor were they sensibly diminished in volume. Other portions were subjected to

electric sparks and discharges in a syphon eudiometer over water, with the same negative results; but when air or oxygen was mingled with the gas, it exploded sharply with heated platinum or the electric spark. When a match was applied to the open end of a tube containing the unmixed gas, it burned rapidly with a pale blue flame, but did not explode. The gas given off during the action of the fused globules on water was not then a mixture of oxygen and hydrogen.

Its freedom from all but a trace of oxygen was ascertained in other ways. To one portion of the gas standing over water nitric oxide was added, but no ruddy fume or yellow coloration showed itself. When phosphorus was introduced into the gas, in one instance it did not smoke, but in the greater number of cases it fumed for a brief period, and occasioned an amount of contraction barely perceptible. The gas appeared to be nearly pure hydrogen. To ascertain if it certainly were so, a portion of it was carefully dried, by chloride of calcium, and transferred to a eudiometer over warm mercury. Dry oxygen was then added, and the mixture exploded. When the whole had cooled, the walls of the eudiometer appeared dimmed by a very thin layer of moisture, but the quantity of gas operated on was too small to admit of visible drops being produced. Another portion of the gas was mixed with half its volume of oxygen and fired by the electric spark. The contraction which followed explosion varied in different experiments, but was frequently such as to leave not more than one-twentieth part of the mixed gases unconsumed. Phosphorus smoked in this residue for a short time, showing that excess of oxygen had been made use of, and left a minute volume of gas which was not diminished by caustic potash, and must have been nitrogen.

It seemed possible that the trace of carbon present even in malleable iron might affect the quality of the gas resulting from the action of the globules of oxide on water, and that carburetted hydrogen, carbonic oxide or carbonic acid might be produced. It seemed desirable to know whether the latter were present or not, as the oxygen might have gone to form them. It was impossible to be certain that carbonic acid was absent, for the gas from the globules being necessarily collected over water, the temperature of which was low, carbonic acid would be retained in solution by that liquid. All that I can say on this point is, that lime-water was not rendered muddy or in the slightest degree opalescent by the gas. It was several times detonated with oxygen over lime-water, but the latter remained quite transparent, so that neither carbonic oxide nor carburetted hydrogen can have been present. In short, the gas evolved from water by the white-

hot globules of oxide of iron, was hydrogen mingled with a small quantity of air, previously no doubt in solution in water.

As only the hydrogen, then, of the water decomposed was obtained, it became necessary to account for the absence of the oxygen. I was tempted for a moment to think it possible that the black oxide of iron might have changed into the red oxide of the same metal, by combining with the oxygen not obtained in the elastic form : *ex. gr.* thus  $2 \text{Fe}_3\text{O}_4 + \text{O} = 3\text{Fe}_2\text{O}_3$ .

But the proto-peroxide of iron is known to be a very stable compound, little if at all prone to become the peroxide ; and it seemed more likely that unoxidized iron might be present in the fused globules, which occasioned the evolution of hydrogen when it came in contact with water. To ascertain this point, portions of the globules were dissolved in dilute muriatic and sulphuric acids, and were found in most cases to evolve hydrogen. Some specimens of the globules gave off not a trace of gas when they dissolved, and must have consisted of the definite oxide ; a point of interest in connection with the fact already mentioned, that globules were frequently observed to drop into water without any bubbles of gas rising from them.

The volume of hydrogen however given off in some of the trials, when the product of combustion was placed in acid, was very considerable. A graduated gas jar was filled with dilute sulphuric acid, and inverted over a small capsule containing 100 grains of the crushed globules, which was placed in a basin also containing dilute acid. By this arrangement the gas was collected and measured at the same time, without risk of mixing with air, or necessity for watching the process, which is a slow one. 100 grains treated in this way gave off 16 cubic inches of hydrogen, corresponding to 9 grains of iron. The experiment was accidentally stopped at this point whilst the gas was still rising in undiminished quantity.

Metallic iron, then, was certainly present in many of the globules, and of this I had direct ocular demonstration. On crushing some of them in a mortar, they were found to separate into a shell of pulverizable oxide, and a core of iron which formed a nearly spherical pellet. In one case 50 grains of the globules were crushed, the pellets separated, and the residue placed in diluted sulphuric acid. It did not evolve a trace of hydrogen in the course of twenty-four hours. The pellets were then added to the same acid, and gave off 12 cubic inches of gas = 13·6 per cent. of iron in the globules\*. The shell of oxide is frequently imperfect or perforated, so

\* In none of the experiments was the thermometer or barometer specially observed, as minute accuracy was not aimed at.

that water or any other liquid penetrates to the iron core, and is subject to its influence. When this becomes known, it need not surprise us that most of the globules should rapidly decompose water. After observing this fact, I tried the effect of thin and thick coils of wire, and found that the latter invariably gave off the greater volume of gas. When the coil is so thin that the metal all oxidizes, no gas is evolved at all. A thick coil indeed furnishes a striking mode of illustrating to a class the principle of Lavoisier's mode of decomposing water, and forms a beautiful addition to the iron-wire experiment.

From these observations then, it would seem that white-hot oxide of iron cannot decompose water in the way white-hot platinum does. But before any conclusion can be drawn from this fact inimical to Mr. Grove's views, or favourable to the opinion that a specific property of the platinum has more to do with the decomposition of water than its mere temperature has, we should require to know how far the two white-hot bodies are to be considered as at the same temperature. In Mr. Grove's experiments, platinum is raised to as high a heat as it can bear without fusing. It must then be elevated to a temperature much above that necessary to make iron white hot, or to fuse its oxide, for our forges can melt iron and its oxides, but do not fuse platinum. It may also be remarked, that bright as the light emitted by burning iron is, it falls short in intensity of that given off by platinum on the verge of fusion. It seems accordingly probable, that during the combustion of iron in oxygen the temperature never rises high enough to confer upon the resulting oxide the power of decomposing water. The question admits of direct decision, by ascertaining whether oxide of iron, heated by the oxy-hydrogen blowpipe to as high a temperature as fusing platinum, acquires the power of decomposing water without appropriating to itself either of its elements. But it would have been an interference with Mr. Grove's own researches to have made experiments of this kind, and I have accordingly left the question undecided.

Meanwhile the experiments I have recorded are of some little interest, as at least showing that not only a white heat, but a high white heat, is essential to the successful performance of Mr. Grove's experiments. Unfortunately, we have not at present any method of measuring high temperatures which admits of ready application or secures great accuracy. "White heat" is in fact a vague expression for a range of temperature, of the extremes in either direction or extent of which we have no very precise knowledge. The power of the eye to measure the relative intensities of the light evolved

by white-hot bodies is very limited, and varies greatly in different individuals. But the experiments I have recorded seem to supply the means of so far at least defining the white heat requisite for the separation of the elements of water, inasmuch as they show that it must at least exceed the temperature necessary for the fusion of malleable iron or its black oxide. If, moreover, the decomposing powers of the electric spark be solely referable to its temperature, we seem entitled to conclude, from the experiments I have detailed, that the heat of the smallest spark that can decompose water is at least equivalent to that of fusing platinum. They appear also to warrant another conclusion. It was suggested by Dr. Leeson and by Mr. Hunt, that the bursting of steam-boilers might occasionally be owing to the metal they consist of becoming white-hot and decomposing water like platinum, with the rejection of both its elements\*. This ingenious suggestion seemed to myself, before making experiments with iron, likely to prove just; but as fusing white-hot iron appears unable to decompose water, otherwise than by combining with its oxygen, it is impossible that the walls of a boiler can ever be raised to a temperature sufficiently high to enable them to separate the elements of water in the way platinum does.

I may now be permitted to make some comments on the rationale of the results obtained by Mr. Grove. That gentleman, if I understand him aright, considers the decomposition of water by white-hot platinum not only, as assuredly it is, a remarkable and unexpected result, but as evidencing on the part of heat a power to produce opposite or dissimilar chemical effects in the same circumstances. He is reported in the *Athenæum* (Sept. 19th, 1846, p. 966) to have "announced his discovery that all the processes by which water may be formed are capable of decomposing water" (p. 966). If by this statement be simply meant, that heat combines oxygen and hydrogen into water, and decomposes water into these gases, it will be admitted to be a just conclusion; but it may be questioned, I think, whether Mr. Grove's experiments add anything to our knowledge of the power of heat to effect chemical changes, except in so far as they supply an additional very remarkable example of its twofold analytical and synthetical agency, which has been so long recognised. Hydrogen, which as a gas is probably the vapour of a very volatile metal, may be compared with mercury, also a volatile substance. If mercury and oxygen be heated together to the temperature of 662° F., they combine and form the red oxide of the metal. If this resulting oxide be raised to a low red heat,

\* *Athenæum*, Sept. 19th, p. 966.

it is decomposed into mercury and oxygen. In like manner, if hydrogen and oxygen be raised together to the temperature of 660° F.\* they unite and form water. If the resulting water be raised to a white heat, it is resolved into hydrogen and oxygen. Both metals (?) present the same phænomena. At one temperature (nearly the same in both cases) combination with oxygen occurs; at a higher temperature, decomposition of the oxide happens. Many other examples might be given in illustration of the same fact. Such cases, however, do not seem to warrant a conclusion as to heat exhibiting anything like a polarity of force, by which I understand the manifestation in opposite directions of opposite powers of equal intensity. At all events, if the opposite effects of different *intensities* of the same agent be considered equivalent to a polarity of action, it is difficult to see what force may not be called a polar one. The decomposing and combining power of heat of different intensities, seems exactly comparable to the opposite effects of different intensities of mechanical impulse.

If two pieces of smooth glass are laid together and struck gently or compressed slightly, they unite or cohere. If the united pieces are thereafter exposed to a sharp blow or to great compression, the union is dissolved, or they are shattered to fragments. Here the same force effects mechanical synthesis and mechanical analysis. But in these contrasted actions, as seems to be the case also in Mr. Grove's experiments, the results are occasioned by a difference in degree of intensity of the same power, not as in the opposite effects of a polarizing force like electricity, by a difference in the kind of power which appears, whatever be its intensity. There is one form, indeed, of Mr. Grove's experiment which at first sight does not appear to admit of the explanation proposed in reference to the other trials—I allude to the decomposition of steam by the electric spark, which is well known to have the power of combining hydrogen and oxygen into water. A similar experiment was made in perhaps a still more instructive form in the latter part of last century by Beccaria†, Pearson and Van Troostwyk, and more recently by Wollaston ‡, in his well-known decompositions of water with guarded poles. In certain of these trials it was found that Leyden jar discharges sent through water, decomposed it till the accumulation of permanent gas left the wires bare; after which the first spark that passed recombined the gases into water, which again covered the wire, when decomposition could

\* Graham's Elements, 1st edit. p. 259.

† Lettere dell' Electrécismo, quoted in Lardner's Electricity, vol. i. p. 78.

‡ Faraday's Electrical Researches, series 3, paragraph 328.

anew be obtained. Here, to appearance, the same agent acting with the same intensity, alternately decomposed and recomposed water. For argument's sake, let it be acknowledged that the heat alone of the spark was the cause of chemical change. Nevertheless it may be questioned, whether it acted with equal intensity in both cases. The electric spark must be conceived, according to the results already given, to be at first at a high white heat, and whilst retaining this temperature we may believe it to possess a power of disuniting the elements of water, and of preventing their union. But as soon as the spark falls to the temperature of 660° F., it loses its power of decomposing water, and, on the other hand, acquires a power of uniting hydrogen and oxygen. Although therefore the spark is always *furnished* of the same intensity, its action may change, and even be reversed, as its intensity diminishes. Moreover, even when the spark is white-hot, it is only the amount of matter directly in its track that will be raised to a white heat. Contiguous portions will have their temperature much lower, so that in the case of hydrogen and oxygen, at some little distance from the route of the spark, the temperature will be 660° F., and there combination will begin, and ultimately extend through the whole mass of gas.

In like manner, when a platinum wire is made white-hot in a mixture of hydrogen and oxygen, it causes their combination. Here we may suppose that union occurs as soon as the temperature of the metal rises to 660° F., and before it acquires a white heat. Or if we were to arrange matters so that the wire should be made white-hot in a vacuum and hydrogen and oxygen afterwards admitted to it, still union of the gases should happen; for although the wire might prevent combination immediately around itself, at no great distance where the temperature was below 700° F. it would compel union. In all such experiments the combining effect of heat will be much more manifest than its decomposing power; not that perhaps the former is in reality greater than the latter, but because flame is propagated through a mixture of hydrogen and oxygen by a series of combustions. The hot wire or the electric spark kindles only the portions of gas immediately adjacent to it, but the combustion of those sets fire to the molecules contiguous to them, and these in their turn to their neighbours, till all are made to burn. Thus the flame travels after the original cause of combustion has ceased to operate directly, and the momentary action of a small spark, or the transient heat of a red-hot capillary wire may suffice to fire an infinitely large mass of hydrogen and oxygen. There is no provision for a similar propagation of decomposition through water or steam when either is made white-hot; the

absolute amount accordingly of disunion of the elements of water occasioned is very small.

If allowance, however, be made for the apparent difference in extent of effect which heat shows in uniting and in disuniting the elements of water, the phenomena otherwise seem referable solely to the intensity of the temperature to which hydrogen and oxygen are exposed. The opposite processes might go on simultaneously, union or disunion being determined simply by the different temperatures to which different portions of the gases were raised. At least it seems not improbable that if a mixture of steam and of hydrogen and oxygen were exposed to electric discharge, decomposition of the steam and combination of the hydrogen and oxygen might be effected by the same spark, provided the volume of steam were not large. In the track of the spark decomposition would occur, so long as a white heat prevailed. When the temperature fell, combination would happen where the spark had passed, if it had not already commenced in the neighbourhood of its direct route. Similar remarks apply *mutatis mutandis* to the action of a hot platinum wire on a mixture of steam with oxygen and hydrogen.

It may be objected to this view, that Mr. Grove decomposes steam in his eudiometer, and obtains a permanent bubble of gas, consisting of hydrogen and oxygen. The bubble however obtained in this way is very small, and could not probably be greatly increased. Mr. Grove has not mentioned how large a volume of hydrogen and oxygen he could obtain in the same eudiometer, by alternately boiling the water till the steam produced caused the liquid to fall below the wire, and allowing the steam to condense till the water rose above the metal. But I venture to say that no large volume of permanent gas could be procured by this process if the same eudiometer were employed many times successively. The combining action of the wire might not take effect on the hydrogen and oxygen when their quantity was small, and they were diluted through a large volume of steam, for in virtue of the law of diffusion, the molecules of hydrogen and oxygen would be separated from each other by molecules of water-vapour; but when the latter diminished in bulk, it seems impossible to doubt that kindling of the gases would occur.

Mr. Grove's experiments then do not appear to prove that heat of the same intensity is able in the same circumstances to form water and to decompose it. When therefore it is stated that water can be produced by the processes that disunite its elements, the word 'process' can only be understood to signify that the general arrangement in both cases is the

same, not that the intensity of the agent called into play, or its mode of action is identical. If this could be affirmed, we should be able to announce as a general proposition, that manifestations of the same force absolutely identical as to quality, quantity and intensity, could produce totally opposite results, which would be tantamount to affirming that unlike effects may flow from the same cause, without any alteration in the qualities or conditions of the latter.

The last observation I would make refers to the curious fact noticed by Mr. Grove, namely, that when a platinum wire is heated white-hot in steam, "in a few seconds a small bubble of gas is formed; but if the action be continued for a week, it does not increase in quantity\*."

Are we to suppose that the wire is at the same time decomposing water around itself, and producing water at a little distance, undoing in one place what it effects in another, so that no permanent accumulation of gas is allowed to take place? This is possible, but I think not likely. The observation made by Mr. Grove seems sufficiently explicable, on the supposition that as soon as the wire is completely enveloped in steam, the thermo-circulatory currents which the high temperature occasions in the vapour prevent it from remaining long enough in contact with the wire to become heated white-hot. The steam probably circulates endlessly around the wire without a trace of decomposition occurring in it. It seems not unlikely indeed that in Mr. Grove's experiments with his eudiometer it was not steam that yielded the hydrogen and oxygen obtained, but the last film of water below the wire, which could not escape from the metal, but tended rather, in consequence of its expansion, to rise towards it, and was thus compelled to acquire a white heat, and to break up into its elements. If this view be correct, an arrangement where a white-hot wire or sheet of platinum foil was kept grazing the surface of water, might be found to effect a continuous decomposition of the liquid in question.

It is no objection to this view that an electric spark decomposes steam readily, for the duration of the spark is so short, that there is no time for the production of thermo-currents, nor any possibility of the steam escaping from the powerful topical action of the discharge. The spark may be compared to fulminating silver, whose action is instantaneous and violent, but quite local,—the heated platinum to gunpowder, the effect of which is cumulative and more general.

\* Athenæum, Sept. 19th, 1846, p. 966.

**XXXIII.** *An account of a Discovery in the Theory of Numbers relative to the Equation  $Ax^3 + By^3 + Cz^3 = Dxyz$ . By J. J. SYLVESTER, Esq., M.A., F.R.S.\**

*First General Theorem of Transformation.*

**I**F in the equation  $Ax^3 + By^3 + Cz^3 = Dxyz \dots \quad (1.)$

**I**A and B are equal, or in the ratio of two cube numbers to one another, and if  $27ABC - D^3$  (which I shall call the Determinant) is free from all single or square prime positive factors of the form  $6n+1$ , but without exclusion of cubic factors of such form, and if A and B are each odd, and C the double or quadruple of an odd number, or if A and B are each even and C odd, then, I say, the given equation may be made to depend upon another of the form

$$A'u^3 + B'v^3 + C'w^3 = D'xyz;$$

where

$$A'B'C' = ABC$$

$$D' = D$$

$$u \cdot v \cdot w = \text{some factor of } z.$$

The following are some of the consequences which I deduce from the above theorem. In stating them it will be convenient to use the term Pure Factorial to designate any number into the composition of which no single or square prime positive factor of the form  $6n+1$  enters.

The equations  $x^3 + y^3 + 2z^3 = Dxyz$

$$x^3 + y^3 + 4z^3 = Dxyz$$

$$2x^3 + 2y^3 + z^3 = Dxyz$$

are insoluble in integer numbers, provided that the Determinant in each case is a Pure Factorial.

The equation  $x^3 + y^3 + Az^3 = 9Bxyz$

is insoluble in integer numbers, provided that the Determinant, for which in this case we may substitute  $A - 27B^3$ , is a pure factorial whenever A is of the form  $9n \pm 1$ , and equal to  $2p^{3i \pm 1}$  or  $4p^{3i \pm 1}$ , p being any prime number whatever.

I wish however to limit my assertion as to the insolubility of the equations above given. The theorem from which this conclusion is deduced does not preclude the possibility of two of the three quantities x, y, z being taken positive or negative units, either in the given equation itself or in one or the other of those into which it may admit of being transformed. Should such values of two of the variables afford a particular solution, then instead of affirming that the equations are insoluble, I should affirm that the *general solution* can be obtained by equations in finite differences †.

\* Communicated by the Author.

† Take for instance the equation  $x^3 + y^3 + 2z^3 = 9xyz$ . The Determinant

*Second General Theorem of Transformation.*

The equation  $f^3x^3+g^3y^3+h^3z^3=Kxyz \dots \dots \dots (2.)$   
may always be made to depend upon an equation of the form

$$Au^3+Bv^3+Cw^3=Duvw,$$

where

$$ABC=R^3-S^3$$

$$D=3R;$$

and  $u.v.w =$  some factor of  $fx+gy+hz.$

$$R \text{ representing } K+6fgh$$

$$S \dots K-3fgh.$$

I have not leisure to show the consequences of this theorem of transformation in connexion with the one first given, but shall content myself with a single numerical example of its applications:  $x^3+y^3+z^3=-6xyz$

may be made to depend on the equation

$$u^3+v^3+w^3=0,$$

and is therefore insoluble.

It is moreover apparent that the Determinant of equation (2.) transformed is in general  $-27R^3$ , and is therefore always a Pure Factorial, and consequently the equation

$$f^3x^3+g^3y^3+h^3z^3=Kxyz$$

will be itself insoluble, being convertible into an insoluble form, provided that  $K+6fgh$  is divisible by 9, and provided further that  $(K+6fgh)^3 - (K-3fgh)^3$  belongs to the form  $n^3.Q$ , where  $Q$  is of the form  $9n\pm 1$ , and also of one or the other of the two forms  $2p^{3i\pm 1}$ ,  $4p^{3i\pm 1}$ ,  $p$  being any prime number whatever.

Pressing avocations prevent me from entering into further developments or simplifications at this present time.

It remains for me to state my reasons for putting forward these discoveries in so imperfect a shape. They occurred to me in the course of a rapid tour on the continent, and the results were communicated by me to my illustrious friend M. Sturm in Paris, who kindly undertook to make them known on my part to the Institute.

Unfortunately, in the heat of invention I got confused about 27.25 is a Pure Factorial: consequently if the solution be possible, since in this case the transformed must be identical with the given equation, this latter must be capable of being satisfied by making  $x$  and  $y$  positive or negative units. Upon trial we find that  $x=1 y=1 z=2$  will satisfy the equation. I believe, but have not fully gone through the work of verification, that these are the only possible values (prime to one another) which will satisfy the equation. Should they not be so, my method will infallibly enable me to discover and to give the law for the formation of all the others.

Here, then, under any circumstances, is an example, the first on record, of the complete resolution of a numerical equation of the third degree between three variables.

the law of oddness and evenness, to which the coefficients of the given equation are in the first theorem *generally* (in order for the successful application of my method as far as it is yet developed) required to be subject. I stated this law erroneously, and consequently drew erroneous conclusions from my Theorems of Transformation, which I am very anxious to seize the earliest opportunity of correcting. I venture to flatter myself that as opening out a new field in connexion with Fermat's renowned Last Theorem, and as breaking ground in the solution of equations of the third degree, these results will be generally allowed to constitute an important and substantial accession to our knowledge of the Theory of Numbers.

26 Lincoln's Inn Fields,  
August 24, 1847.

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*XXXIV. Experiment made at the Kew Observatory on a new  
Kite-Apparatus for Meteorological Observations, or other  
purposes\*.*

M R. W. R. BIRT (on the 14th of this month) took some kites, &c. to the Kew Observatory, for the purpose of endeavouring to ascertain how far it might be practicable to measure the force of wind at various elevations by their means, and (in the mere manipulation of his experiments) was assisted by Mr. Ronalds. After several trials, &c. they agreed that the sudden variations, horizontal and vertical, in the position of the kite, the great difficulty of making a kite which should present and preserve a tolerable approximation to a plane, that of measuring, with sufficient accuracy, at any required moment, its inclination, and lastly, the influence of the tail, would always tend to render the observation somewhat unsatisfactory. Mr. Ronalds then proposed to try the following method of retaining a kite in a quasi invariable given position. Three cords were attached to an excellent hexagonal kite of Mr. Birt's construction: one in the usual manner, and one on each side (or wing). The kite was then raised as usual; the two lateral cords were hauled downward by persons standing at the apices of a large equilateral triangle (described upon the ground) until the ascending tendency became considerable (even when the force of the wind was at its minimum), and the three cords were made fast to stakes or held in the hand. He had entertained no expectation of the favourable result of this simple and obvious contrivance. The place of the kite did not seem to vary so much as one foot in any direction, and it really appears to him probable that a very large kite or kites might be employed in this kind of manner often and very

\* Communicated by Mr. Ronalds.

cheaply as a substitute for a captive balloon in meteorological inquiries, or even (on a very extensive scale) for other requirements in military science, &c. An anemometer, a thermometer, an hygrometer, &c. of some registering kinds, &c., might be hauled up and lowered at pleasure (like a flag) by a person standing in the centre of the triangle (above referred to), and by means of a line passing through a little block attached to the kite. The cords and kite should of course be of pure silk, for the sake of lightness, combined with extreme strength, and the size and thickness in some measure adapted to the breeze or lighter air. The silk might be advantageously covered with a very light coat of elastic varnish.

*XXXV. On Transformations produced by Catalytic Bodies.*  
By LYON PLAYFAIR, Esq.\*

BERZELIUS rendered a most useful work to science, when he collected into one class those varied phenomena of chemical action resulting from causes certainly very different from the ordinary manifestations of those affinities, which produce combinations or promote decompositions. This philosopher believes the power †, which causes decomposition without the acting body participating in its result, to be a distinct electro-chemical agency different from other recognised powers, and he named it the "Catalytic force." According to this view, catalytic bodies do not act by chemical affinity, but they excite inherent affinities in other substances, in consequence of which new combinations or decompositions ensue.

Mitscherlich ‡, adopting this view, considered a number of catalytic decompositions in detail, and showed the important influence exerted by the state of surface of bodies in favouring this peculiar action, which he denominates decomposition by *contact*. The examples, adduced in this interesting memoir, of the favourable action of an extended surface upon combination, fully prove that the physical condition of bodies exercises an important influence upon the action of this force; but they do not remove the necessity for studying the force itself, as it may either be a *vis occulta*, entirely distinct from powers already recognised, as Berzelius supposes, or may be modified forms of those in continual operation.

Liebig§ views the catalytic power as a dynamical action

\* Communicated by the Chemical Society; having been read April 5, 1847.

† *Jahresbericht*, xv. 237.

‡ Taylor's Scientific Memoirs, Part xiii.; or Pogg. *Ann.* xxxi. 281.

§ Liebig's Chem. of Agriculture, 4th edit., p. 284.

on the atoms of a complex molecule, conceiving that the activity of the atoms of a body in a state of motion may be communicated to those of another body in a state of rest. The atoms of a compound, according to this view, if in a state of exact statical equilibrium, arrange themselves according to new affinities, when the *vis inertiae* is overcome by motion. In proof of this view, Liebig carefully examines a large number of decompositions, and accounts for some of the most difficult transformations in organic chemistry.

But there are many instances, to which I shall have to draw attention in the present memoir, where catalytic decompositions ensue when there is no intestine motion in the atoms of the exciting body ; and hence we cannot do more than consider motion as favourable to the development of dormant affinities, in a manner similar to the surface action described by Mitscherlich. The power of peroxide of hydrogen and of pyruvic acid to reduce oxide of silver is certainly a singular phenomenon, and appears favourable to Liebig's views ; but the cause of the original decomposition of the peroxide of hydrogen cannot be ascribed to motion, as the atoms of the oxide of silver are not in that state, and those of the peroxide of hydrogen either not at all or only slightly so. Neither will it suffice to suppose that the escape of gas during such decompositions is due to the presentation of angular points from which the gas may escape\*, because solutions of alkalies equally effect the decomposition, according to Thenard †. The cause, therefore, which enables certain substances to hasten the decomposition of such bodies as peroxide of hydrogen or persulphuret of hydrogen, although favoured by the state of surface and by motion, is independent of mere physical condition.

In further proof of the importance of motion in causing combination or decomposition, Liebig cites the favourable effects of agitation on the precipitation of potash by tartaric acid. It may be questioned, however, whether this is not either a mechanical breaking up of a combination or the simple effect of cohesion. Thus when water is saturated with a gas, a brisk agitation with a rod causes the separation of bubbles of gas previously dissolved. The mechanical force may here be supposed to have broken up the compound molecule of water and gas by detaching the former, and thus enabling the gas to escape by its elasticity. In the precipitation of potash by tartaric acid, cohesion may effect the same result that elasticity does in the case of gas, the agitation knocking off the

\* *Ann. der Pharm.*, ii. 22.

† *Ann. de Chim. et de Phys.*, xlvi. 79.

atoms of water which are feebly attached. In fact we know that the addition of alcohol equally aids the precipitation, the action here being a chemical separation of the water, as in the other it is mechanical. The diminished solubility of the salt, after it has been influenced by cohesion and separated from water, has its counterpart in many similar instances; for example, in the small solubility of anhydrous sulphate of iron. The effect of agitation on a solution of sulphate of soda, saturated while hot and allowed to cool, I ascribe to the same cause. The supposed effect of cohesion or elasticity in these cases is nothing more than that constantly observed in ordinary phenomena, when the gravity of a substance is different from that of the medium in which it exists. The vesicles of water in the atmosphere may be so small that they float in it and produce fogs; but when aggregated together by the motion of the air, they form drops, which precipitate to the ground with a rapidity proportionate to their size: the converse of this is also true. Thus, the particles or aggregated atoms of carbonic acid in water may be so very small, that, with the slight affinity of the latter added, they may be enabled, when in a state of rest, to remain without resuming their elastic form; but agitation causes a larger system of aggregated atoms, and the gas now escapes in small bubbles.

The first instance of cohesion applies in the precipitation of tartar. At the moment of formation the particles may be so widely apart, that, aided by their slight affinity for water, they remain without aggregating to any considerable extent. Brisk agitation, and the presentation of an extended surface, effect their aggregation and cause a speedy precipitation. It may be that these are really instances of combination favoured by motion; but presuming that they are, the general argument is not affected, that other decompositions perfectly analogous are produced where the exciting body is in a state of rest.

The third theory of these decompositions is, that catalytic bodies act by exerting a feeble chemical affinity on one of the constituents of the body decomposed. This view was introduced by Mercer \*, and supported by several very ingenious experiments communicated to the British Association at its meeting in Manchester. One of these was, that protoxide of manganese had the singular power of hastening the oxidation of starch in nitric acid †. The metallic protoxide, from its

\* Reports of British Association, vol. xi. 2d Part, p. 32.

† The experiment is easily made by dissolving 1 ounce oxalic acid in  $\frac{1}{2}$  a pint of water at  $180^{\circ}$  F., and adding to this 1 oz. colourless nitric acid of

disposition to pass into the state of peroxide, aids the oxalic acid to decompose the nitric acid, the united affinities of both being able to accomplish what neither by itself could do. The protoxide remains unaffected at the end of the experiment, because, under the circumstances (the presence of acid), it cannot gratify its desire to become peroxide, and, therefore, it passes over its oxygen to the carbon, which escapes as carbonic acid. Mercer cited, as further examples, the action of protoxide of copper in eliminating oxygen from a solution of hypochlorite of lime, and of peroxide or binoxide of nitrogen in commencing the oxidation of a mixture of protochloride of tin and nitric acid. Mercer implied by these instances, that catalysis is an affinity of the catalytic agent for an element in the body acted upon, that affinity being feeble and incapable of gratification under the circumstances.

It would be advantageous to science if we could arrange under a known power the cases of decomposition which appeared so mysterious as to induce the great Berzelius to ascribe them to the action of a new force. It may not be possible in the present state of our knowledge to comprehend the whole of the instances observed, but, if most are included in one category, we have a right to suppose that the others may be embraced as our knowledge progresses. I shall therefore endeavour to show that many catalytic decompositions are merely cases of chemical affinity exerted under peculiar conditions.

In no instance of chemical union does there seem to be such a complete gratification of affinity as to suppress the attractions of the elements. The inherent affinities still remain more or less powerful, for, if it were not so, the compound would be permanent under all circumstances and not liable to further change by the action of external agents. When manganese unites with 1 atom of oxygen, the affinity of the metal for oxygen is not wholly merged, but is still strong enough to attach to itself 1, 2 or 3 atoms more oxygen. When the oxide is one of the lowest of the series, this affinity exhibits itself in a *basic* power by attaching itself to any complex highly oxygenized molecule, such as the oxygen acids, or of radicals playing the part of oxygen. When, on the other hand, the manganese or other radical becomes highly oxygenized, we find it possessing *acid* properties, that is, the

1.30 sp. gr. No action ensues on this mixture, but it immediately commences on the addition of a protosalts of manganese, which for simplicity may be the oxalate or nitrate. The action is also strikingly shown by heating a mixture of oxalic acid until the action commences, then diluting it till all action ceases. A little protosalts of manganese now added to the solution causes an immediate renewal of the oxidation.

additional atoms of oxygen, being less firmly attached, are capable of gratifying the disposition of a less oxygenized atom (the base) to attach itself to a higher oxide, or, to use the convenient phraseology of Graham, the base becomes zincous to the acid, which is now chlorous.

On heating the nitrates, nitric acid is not given off, but  $\text{NO}_4 + \text{O}$ . The decomposition readily results from the dis-position of the base to appropriate more oxygen and pass into the higher oxides. If the base be oxide of nickel, the oxygen becomes attached to the oxide and remains ; if, however, an oxide which has but a feeble affinity for oxygen at an elevated temperature, the elasticity of that element is able to overcome the affinity, which succeeded in breaking up the nitric acid. The final action is so obviously dependent upon the oxygenous part of the acid, as to make Schönbein believe that salts contain peroxides ready-formed ; thus that  $\text{NO}_5$ ,  $\text{HO} = \text{NO}_4 + \text{HO}_2$ , or  $\text{PbO}$ ,  $\text{NO}_5 = \text{NO}_4 + \text{PbO}_2$ . This however is an unnecessary supposition, the previous view accounting sufficiently for the decomposition of a nitrate, so as to produce  $\text{NO}_4$  and  $\text{O}$ . Admitting this view to be correct in the expression that the preponderating quantity of a chlorous element in an acid renders the latter chlorous to a base, the mechanical attachment being to the chlorous element, we can understand why the number of atoms of oxygen in a base should regulate the number of atoms of acid attached to it. Thus  $\text{RO}$  presents only one chlorous element of attachment to the acid, and therefore the latter adheres to it in one proportion ; whereas  $\text{R}_2\text{O}_3$ , which possesses three atoms of a chlorous element equally distributed round a zincous nucleus, presents three points of attachment, and therefore produces a salt  $\text{R}_2\text{O}_3, 3\text{A}$ . This view in result gives all the simplicity of the acid radical theory, both views entertaining the idea that the oxygenous atoms of the base and acid are attached to each other. We have certain instances, as for example  $\text{KO}$ ,  $\text{ClO}_5$ ;  $\text{PbO}$ ,  $\text{NO}_5$ , where the elastic atoms of oxygen combine as closely together as non-elastic atoms, such as lead or silver.

Although to aid conception we may suppose the atoms of oxygen of the base and of the acid to be in mechanical connexion, the true arrangement is probably not so, seeing that in a base there is always a part more zincous than the oxygenous atom, although the base as unity is zincous to the acid. We see many instances in chemistry of union of atoms in pairs, or what may be called *dual affinity*. This Graham\*

\* Trans. Royal Soc. Edin. vol. xiii.; Phil. Trans. 1837, p. 47 *et seq.*; Phil. Mag. Third Series, vol. xxiv. p. 401 *et seq.*

has proved to be the case with regard to atoms of water, and we know of numberless instances in the case of oxides. Thus  $\text{RO}$  uniting with oxygen forms  $\text{RO}_2$ . In this case  $\text{RO} + \text{O}$  corresponds to  $\text{RO} + \text{A}$ , the acid here representing the chlorous element from its oxygenous character. It is not necessary to suppose that  $\text{A}$  and  $\text{O}$  are associated in one continuous line, the probability being that the molecule may really be represented by  $\text{ARO}$ . Thus also in  $\text{R}_2\text{O}_3$ , where the  $\text{O}_3$  are probably grouped equally round  $\text{R}_2$ , there is room for three more of a chlorous element to gratify the dual affinity, and the general formula  $\text{R}_2\text{O}_3$ ,  $3\text{A}$  is the result, the  $3\text{A}$  here representing three of a simple chlorous element. The result, as regards affinity, will still however be the same, the whole depending upon the attraction of the central nucleus  $\text{R}$ . It is therefore only for simplicity of expression in studying the phænomena of catalysis, that I view the atoms of oxygen of an acid as associated in mechanical continuation with the atoms of oxygen of the base, the *effect* being represented by this expression : the whole views of molecular or atomic constitution of bodies are in my opinion only convenient fictions to enable us to study the forces themselves, and the conception of a mechanical arrangement I only adopt as expressive of the manifestations of powers residing in matter.

To show that the tendency of bases to  $\text{NO}_5$ , even without being combined, is to attach themselves to the oxygenous part of the acid, a curious phænomenon observed by Mercer may be cited.

A portion of alumina may be taken and placed at the bottom of a vessel containing warm  $\text{NO}_5$ ; no action ensues, except partial solution; a slip of calico coloured in indigo-blue may now be introduced into the mixture, and remains unaffected in the clear acid, but is immediately discharged when pressed with a glass rod into the alumina. Here the alumina acts by placing the oxygen of the nitric acid in a state of tension without however succeeding in decomposing it, but the moment an assistant affinity comes into play, that state is shown by the decomposition of the nitric acid and oxidation of the indigo. The alumina in the presence of the acid could not oxidize (in fact, we know of no higher oxide), and therefore the indigo appropriates the oxygen. I find that various other oxides, such as calcined  $\text{Cr}_2\text{O}_3$  and  $\text{SnO}_2$ , have the same power, the latter showing this disposition more strongly than any of the other oxides. The best mode of trying these experiments is to heat a certain quantity of nitric acid, and then dilute it till indigo cloth ceases to be bleached. The oxide of tin is now added and allowed to fall to the bottom. On in-

troducing a slip of indigo-blue calico, the portion in the clear acid will be found to remain unaffected, while that in contact with the insoluble oxide will be bleached in a few seconds. That this decoloration of the indigo is due to the assistant affinity of another body acting in the same direction, *i. e.* also having a disposition to unite with oxygen, may perhaps best be shown by the following experiment:—Warm nitric acid is diluted to such extent that it just ceases to discharge indigo-blue calico; it is then divided into two portions, with slips of coloured calico in each, and through one of these bioxide of nitrogen is passed. In the latter the indigo becomes quickly bleached, while it remains unaffected in the former, the action obviously being due to the accessory affinity of the nitric oxide for more oxygen. In the same way indigo-blue is discharged during the decomposition of a nitrate by heat, other kinds of organic matter being oxidized under like circumstances; in these instances the decomposition of the nitric acid is much facilitated,—1. by the affinity of the base for oxygen; 2. the affinity of the organic matter for oxygen, which unites with it at the elevated temperature. There are many similar instances of this kind, where the behaviour of  $\text{NO}_2$  or  $\text{NO}_4$  as an assistant is too clearly contrasted with the action of other bodies to permit mistake. Thus urine when kept is unfit for the preparation of urea, that substance having been converted into carbonate of ammonia during the action of the air upon the mucus or colouring matter contained in the fluid. Colourless nitric acid unites with urea and may be heated with it without decomposition; but nitric acid containing any of the lower oxides of nitrogen, such as  $\text{NO}_2$  or  $\text{NO}_4$ , immediately decomposes urea into carbonic acid and ammonia\*. We cannot conceive that a lower oxide can more readily oxidize urea than a higher oxide, and hence we can only view the  $\text{NO}_4$  as aiding the urea to oxidize itself, as the mucus does in urine. In the same way, the action of pure nitric acid on colourless uric acid is to form alloxan, if the operation has been conducted so as to prevent the formation of nitrous acid ( $\text{NO}_4$ ) during the oxidation. But if  $\text{NO}_4$  has been evolved, or if the colouring matter of the urine be still contained in the uric acid, the products are only carbonate and oxalate of ammonia. The colouring matter of the urine and  $\text{NO}_4$  are thus seen to possess a similar action, which is exactly the same as that of protonitrate of manganese on a mixture of starch and nitric acid, no oxalic acid being formed in the presence of this salt, the only product of

\* A solution of urea in nitric acid is immediately decomposed with lively effervescence when a little  $\text{NO}_2$  is passed through it.

oxidation being carbonic acid. The  $\text{NO}_4$  or  $\text{NO}_2$  acts in these cases clearly by aiding the compound ready to oxygenate, but which, under the conditions, has not sufficient power to decompose the nitric acid without additional aid. The same explanation probably applies to the singular discovery of Professor Graham\*, that the addition of  $\text{NO}_4$  to non-accendible phosphuretted hydrogen renders it inflammable. In this case the two combined affinities produce the union of oxygen with one of the bodies. The presence of the small quantity of another compound of phosphuretted hydrogen in the spontaneously accendible gas, as described by Leverrier† and by Thenard‡, may probably act in the same manner.

The action of this compound ( $\text{PH}_2$ ) corresponding to amiodgen ( $\text{NH}_2$ ) may be conceived so to disturb the attraction of the phosphorus to the hydrogen in the gas  $\text{PH}_3$  as to produce the inflammability. Both the elements of this gas are highly combustible, uniting with oxygen at a low temperature. Their mutual attractions are sufficiently strong to prevent the oxygen breaking up this union; but when the second body is present, the desire of  $\text{PH}_2$  for another atom of hydrogen may be supposed so far to draw the third atom of hydrogen from the  $\text{PH}_3$ , that oxygen has now the power to unite with the two inflammable elements. In disturbing the existing equilibrium, it is presumed to act just as a spark would do by elevating the already strong affinities of the two elements for oxygen. When a solution of hypochlorite of lime is poured into a solution of muriate of ammonia in excess, a very pungent volatile compound results, which has no bleaching properties, and therefore does not contain hypochlorous acid. The decomposition is expressed by the equation  $\text{NH}_4\text{Cl} + \text{CaO}, \text{ClO} = \text{NH}_2\text{Cl} + 2\text{HO} + \text{Ca Cl}$ . The volatile compound  $\text{NH}_2\text{Cl}$  has an affinity for hydrogen in order to pass into  $\text{NH}_4\text{Cl}$ . This body was well-fitted to test the view of the cause of the inflammability of phosphuretted hydrogen (even supposing  $\text{PH}_2$  is not spontaneously inflammable, as it is stated to be by Thenard). On placing gas (which had entirely lost its inflammability by standing several days over water), in contact with the above mixture, in about an hour it acquired the property of smoking strongly in the air, although it did not inflame spontaneously. This showed that the affinity of  $\text{PH}_3$  for oxygen was much elevated, although the attraction was not sufficient for inflammation.

\* Trans. Royal Soc. Edin. vol. xiii. p. 5.

† Ann. de Ch. et de Phys. lx. 174.

‡ Comptes Rendus des Séances de l'Académie des Sciences, t. xviii. pp. 252, 914; t. xix. p. 313.

There cannot be any doubt that the atoms of a body may be placed in a greater or less degree of tension by varying conditions. The experiments of Mr. Joule\* and myself on Allotropism have fully proved that the space occupied by the same body alters under different circumstances. It is therefore not an unreasonable assumption that the affinity of one body for a particular element may be sufficiently great to produce a tense state of the atoms without effecting decomposition†: hence the added affinity of a second body acting in the same direction may cause that change which each alone could not effect. Anything that disturbs the state of statical equilibrium in such a body will often effect its decomposition.

This accessory affinity is recognised when both bodies enter into union. Charcoal and chlorine decompose alumina at a red heat, though neither can do so separately. In the same way Boudault‡ has shown that a mixture of potash or soda and red prussiate of potash oxidizes various metallic oxides, while Mercer has for many years made use of this mixture to discharge indigo-blue on calico§. Red prussiate of potash ( $\text{Fe}_2\text{Cy}_6\text{3K}$ ) has a great disposition to attach to itself another atom of potassium to become yellow prussiate of potash ( $\text{Fe}_2\text{Cy}_6\text{4K}$ ). It cannot gratify this desire without aid; but when assisted by a substance having an affinity for the oxygen of the potash, and capable of appropriating it, decomposition follows. There are often cases in which the body exercising the accessory affinity may be unable to effect the union, either by the influence of unfavourable chemical conditions or of cohesion or elasticity. Thus, in the case with which we first started, the affinity of protoxide of manganese for oxygen aids in the decomposition of nitrate of protoxide of manganese, and sesquioxide of manganese remains. If the temperature during the decomposition

\* Memoirs of Chemical Society, vol. iii. p. 93.

† The alteration in volume is best seen in those oxides which contract and increase in specific gravity by the application of heat, for example, when the brown oxide becomes the green oxide of chromium. The two oxides must have a different molecular constitution, and this may be supposed to result from the elastic powers of one of its elements and the cohesive force of the other. The first effect of heat on oxide of chromium must be to expand the atoms of oxygen, and removing them further from the two atoms of chromium, permit the cohesive attraction of the latter to be gratified. Hence the compound acquires properties dependent upon cohesion, such as indifference to union and diminished solubility.

‡ *Journal de Pharmacie*, tome vii. 437. [Phil. Mag. Third Series, vol. xxvii. p. 307.]

§ Phil. Mag. Third Series, vol. xxxi. p. 126. In justice to Mercer, although this does not remove Boudault's claim of priority of publication, I cannot refrain from stating that the former chemist pointed out to me the oxidizing powers of the prussiates four or five years since.

be elevated, the oxygen resumes its elastic state and refuses to form this higher oxide, as in fact we know is the case in Mercer's experiment with oxalic acid and nitric acid, where the presence of hot  $\text{NO}_5$  is an unfavourable chemical condition to the existence of  $\text{Mn}_2\text{O}_3$ , and therefore it is not formed, but in its stead the oxygen is passed over to the organic matter, which is able to unite with it under the circumstances. A similar instance of the effect of such conditions is seen when the peroxides of copper, manganese or lead, are thrown into a solution of bleaching powder. The affinity of these oxides for an additional quantity of oxygen enables them to decompose the hypochlorite of lime, converting it into chloride of calcium. When the protoxides are used, this liberated oxygen unites and converts them to peroxides. The latter themselves have sufficiently strong affinity for oxygen to cause the decomposition to proceed; but not uniting with it, pure oxygen is given off in the gaseous state. Here elasticity has come into play, and being more powerful than the feeble chemical affinity, causes the oxygen to escape as a gas. When the solution is cool the gas goes off in a succession of small bubbles; but when hot, the escape is tumultuous, the heat aiding the oxygen to enter into the elastic state\*. A solution of chloride of lime evolves oxygen slowly at the boiling-point; but the decomposition is much accelerated by the accessory agents referred to.

The action of certain oxides upon peroxide of hydrogen is exactly similar to that on a solution of hypochlorite of lime. Thus peroxide of manganese, the protoxides of cobalt and lead, minium, peroxide of iron, and the protoxides of nickel, copper and bismuth, all exert this action on peroxide of hydrogen with a force indicated by their order†. In none of these cases does the oxide unite with a further proportion of oxygen. The violence of the action is however in proportion to their power of uniting with more oxygen. The first five oxides in the list have higher oxides of definite composition and of a certain degree of stability, with the exception of ferric acid; while the protoxides of copper and bismuth, although possessing the power of uniting with more oxygen, do not present superior oxides of a marked character. We should have

\* The best mode of instituting the experiment is to make a mixture of chloride of soda and caustic soda, heat this to a temperature near ebullition, and add sulphate of copper. The oxide of copper precipitated in the fine state of division causes such a copious evolution of oxygen gas that the contents are apt to be thrown out of the vessel: a mixture of chloride of lime and lime, or the ordinary unfiltered bleaching-powder of commerce, are also well-fitted to show the action.

† Thenard's *Traité de Chémie*, 6th edit. vol. i. p. 216.

expected the oxides of nickel and cobalt to have exerted the same power, but from Thenard's description of the former being in the state of a black powder, it may have been the oxide of increased specific gravity, to which attention has already been drawn\*. In all these cases the affinity is supposed to be sufficiently strong to break up the atoms of a body yielding to the slightest disturbance of its state of statistical equilibrium. Two affinities are at play in these decompositions, viz. the attraction of the metallic oxide for oxygen and that of the water for the same body; both these affinities resist the union, and therefore, elasticity coming into operation, robs both oxides of the gas. The affinity causing the decomposition is so slightly preponderating in its influence, that a second cause coming into operation is quite sufficient to alter the conditions under which it was originally exerted, and to draw one of the elements of the body acted upon beyond the sphere of its affinity.

The balance of affinities in all such cases is so near that we not unfrequently find apparently contradictory effects resulting from their gratification. Thus the addition of oxide of silver to peroxide of hydrogen expels oxygen from the latter, but at the same time it is robbed of its own oxygen and reduced to the metallic state. In this case we have two feeble compounds instead of one, with affinities very nearly balanced, and with atoms so tense as to yield readily to the first disturbing cause. We can scarcely adopt as sufficient the explanation of Thenard and Mitscherlich†, that the reduction is due to the elevation of temperature accompanying the decomposition, because even when that is lowered by the addition of much water to the peroxide of hydrogen, the silver still becomes metallic.

It is a point yet undetermined, whether a lower oxide is to be considered as unity to a higher oxide, or whether all the atoms of oxygen are held by equal attractions. We know that tartaric acid is able to separate potash from nitric acid in forming a bitartrate, and yet acetic acid is sufficient to remove the second atom of potash from the neutral tartrate. But in a bibasic acid, like tartaric acid, it may be either atom of potash that is abstracted, and the superior affinity for the remaining one may be owing to attractions resulting after the expulsion of the first. Thus  $MnO_2$  may have its atoms of oxygen distributed round the central nucleus Mn, and held by equal attractions, and the stability of the red oxide produced by its calcination does not show that it pre-existed

\* Memoirs of the Chemical Society, vol. ii. p. 384, and vol. iii. p. 81.

† Poggendorff's *Annalen*, lv. 321.

in the black oxide, but merely that the attraction became stronger when one of the elements which divided it was removed. If it be admitted that the attraction of a radical for oxygen is equally divided between all the atoms of that element associated with it, the action to which we have alluded becomes comprehensible. In an oxide we have the attraction of affinity opposed by the elasticity of its oxygen and by the cohesive force of the metal. If  $a$  be the attraction of the central nucleus or radical,  $c$  the cohesive force of the metal, and  $e$  the elasticity of the oxygen, then the molecular formula of a protoxide will be  $\frac{a}{c+e}$ , of a sesquioxide  $\frac{2a}{2c+3e}$ , and of a binoxide  $\frac{a}{c+2e}$ . Now if, as in oxide of silver, the  $a$  and  $e$  are nearly equal, or the  $a$  only slightly preponderating, and the  $c$  or cohesive force very powerful, we can readily conceive that the added force of a second  $e$  may overcome the small amount of preponderating force in favour of  $a$ . Thus, when oxide of silver is placed in contact with peroxide of hydrogen, its affinity for more oxygen is sufficient to draw the second atom of oxygen beyond the sphere of attraction of H, and deliver it over to its own elasticity. But in doing this the attraction of silver for oxygen has been divided between its own oxygen and that of the peroxide of hydrogen. Scarcely at any time capable of retaining its own oxygen, this division of its attractive force has been fatal to the existence of its oxide, and the water *in statu nascens* at the same time exerting an affinity for the oxygen just ready to escape; all these causes combined result in the reduction of the silver\*.

When pyruvic acid is in contact with oxide of silver, it unites and forms a salt; but when acting on carbonate of silver, a certain quantity of oxygen also leaves the oxide during the escape of carbonic acid, and metallic silver remains†. As Liebig ‡ suggests, motion may aid this result; but were this the only explanation, we should expect that

\* During the passage of this paper through the press, Mr. Brodie, in a lecture at the Royal Institution, showed that peroxide of potassium reduces chloride of silver, the two atoms of oxygen passing off in the gaseous state, while chloride of potassium and metallic silver remain behind, a singular decomposition, when the behaviour of potash is remembered. But the action is strictly the same as that here described; the atoms of oxygen, being liberated at the same time, are presented to the silver, which, dividing its attractive force between them, is not able to overcome the influence of elasticity of the oxygen and its own cohesion, and therefore remains in a metallic state.

† Berzelius, *Lehrbuch der Chemie*, fifth edit. vol. iv. p. 231.

‡ Chemistry of Agriculture, 4th edit., page 283.

silver would constantly be reduced during the action of other feeble acids on carbonate of silver. If, however, we suppose that the pyruvic acid,  $C_6 H_6 O_5$ , from its affinity for more oxygen, exerts an attraction for that element at the moment of the liberation of the carbonic acid, the decomposition would be similar to those we have already considered, especially if the previous view of the molecular constitution of salts be admitted. In that case the oxygen of the oxide being attached to that of the carbonic acid, will be made highly tense during the escape of the latter, and may therefore be detached by a very feeble force, its elasticity finally overcoming the weak affinity. An extension of the explanation however strikes me as more probable, but it would be premature to insist upon it without being supported by experiments which I have not yet been able to conclude.

The action of metals and of charcoal on peroxide of hydrogen may be explained by the same feeble affinity. Alkalies also, from their attraction for oxygen, as indicated both by their capability of uniting with more oxygen and by their basic power or disposition to attach themselves to a compound behaving as an oxygenous or chlorous element, favour the decomposition of  $HO_2$ , while acids, on the other hand, render it more stable, perhaps, as Thenard himself suspected\*, from there being an inferior oxide ( $H_2 O_3$ ?). In this instance the elasticity of the oxygen tends to conceal the play of affinities by preventing combination.

When the acting body is present in large quantity, or exhibits an increased surface, the action goes on with proportionate rapidity. Thus, when nitric acid is in contact with starch, the action is moderate until a certain quantity of peroxide of nitrogen has been evolved by decomposition, after which it proceeds with a violence difficult to control. The peroxide of nitrogen surrounding every particle of starch aids it in the decomposition of the nitric acid. That this is the real cause of the phænomenon may be proved by the following simple experiment. Nitric acid is heated with starch to a temperature at which the action has a tendency to commence but has not yet begun. A stream of  $NO_4$  or  $NO_2$  is then passed through the liquid, when action immediately begins with an activity proportionate to the quantity of gas added. The elevation of temperature due to the progressive action influences the decomposition, by causing the atoms of nitric acid to become more tense. Exactly the same accessory affinity is used by the manufacturer of oxymuriate of tin, when he adds a fragment of tin to the mixture of chloride of tin and

\* *Traité de Chimie*, p. 211.

nitric acid. The tin eliminating some nitric oxide quickens the action, which commences with difficulty with pure nitric acid; nitric oxide gas passed through the solution answers the same purpose.

This accessory affinity also enables oxide of copper or peroxide of manganese to evolve copious streams of oxygen from chlorate of potash in a state of fusion. The heat of fusion decomposes the compound slowly, but on adding a body having an affinity for the element acted upon by the heat (oxygen), the decomposition proceeds with greatly increased rapidity. We cannot ascribe this action to the presentation of points from which the gas may escape, as in the lowering of the temperature of ebullition by particles of sand, because silica has no influence in accelerating this decomposition\*.

In the examples previously given we have the decompositions aided by the tendency of one of the bodies to assume the elastic form. But when the body acted upon has two elements, one of which is influenced by elasticity, the other by cohesion, we find it peculiarly liable to be acted upon by external agents. Persulphuret of hydrogen is a compound of this class, and has been closely studied in its decompositions by Thenard†. The same bodies which decompose peroxide of hydrogen act catalytically upon this sulphuret. The decomposition cannot be due to points for the escape of gas, as suggested by Liebig‡, to explain the decomposition of peroxide of hydrogen, because solutions of the alkalies act with equal power. The sulphurets, especially those of the alkaline metals, decompose it very readily. As in the case of peroxide of hydrogen, the acids afford stability to its sulphur analogue. In the view of acids given, they are supposed to have become chlorous or electro-negative, representing and behaving as oxygen, and therefore exerting no affinity, we should anticipate that they would not show any disposition to break up an oxygenous compound or its analogue of sulphur. Another instance of accessory affinity is seen in the nitrosulphates§; the formula ( $\text{RO}_2\text{SO}_2 + \text{NO}_2$ ) given by Pelouze to these compounds does not allow us to understand their decompositions, which however becomes intelligible if we view nitrosulphuric acid as nitric acid, in which the fifth atom of oxygen has been replaced by one of sulphur ( $\text{RO}_2\text{NO}_4\text{S}$ ). In this acid we have two elements—the nitrogen and the sulphur—sharing the oxygen, their mutual affinities being nearly balanced when the acid is united with an al-

\* Taylor's Scientific Memoirs, vol. iv. p. 9.

† Ann. de Ch. et de Ph. xlvi. 79.

‡ Ann. de Ch. et de Ph. lx. 151.

† Ann. der Pharm. ii. 22.

kali, although in a free state, the sulphur exhibits a superior affinity, as shown by the decomposition which then results,  $\text{NO}_4\text{S} = \text{NO} + \text{SO}_3$ . Now any substance which acts as an accessory to the sulphur by aiding the withdrawal of oxygen from the nitrogen decomposes it. This instability is especially exhibited in  $\text{NH}_4\text{O}$ ,  $\text{NO}_4\text{S}$ ; the 3 atoms of hydrogen of the ammonia in their attraction for oxygen introducing another affinity, which accelerates decomposition. And, in fact, we do find that the same agents which so readily decompose the oxygenous compounds, chloride of lime and peroxide of hydrogen, do equally cause the disruption of nitrosulphate of ammonia into protoxide of nitrogen and sulphate of ammonia. Alkalies are an exception to this rule, as they render the nitrosulphates more stable, while they make the peroxide of hydrogen prone to decomposition; but the cases are different, the latter substance having none of the properties of an acid.

The basic character of alkalies, defined as their power of uniting with more oxygen, or with an acid playing the part of an oxygenous element, is illustrated by several curious decompositions. Thus, though grape-sugar reduces sulphate of copper with ease, cane-sugar alone does not readily do so, but when mixed with potash and boiled with the salt, suboxide of copper is produced, as in the mode of preparation of that oxide suggested by Boettger\*, or the reduction of chloride of silver as proposed by Levolt†. Here the disposition of the organic matter to unite with oxygen is able to gratify itself when aided by the accessory affinity of the potash for oxygen. That the potash in this state acts by aiding the oxidation, is seen by heating  $\text{Cu}_2\text{O}$  with a solution of caustic potash, exposed to the air, when it oxidizes much more rapidly than when boiled with water alone‡. When suboxide of copper is dissolved in ammonia it oxidizes with surprising rapidity. In this instance the hydrogen of the ammonia adds to its disposition as an alkali to absorb oxygen. The quick oxidation is not merely due to the fact of

\* *Ann. der Pharm. und Chemie*, xxxix. 176.

† Berzelius, *Jahresbericht*, vol. xxv.

‡ This experiment may be simply made as follows:—Three shallow evaporating basins of the same size and form, each containing the same quantity of suboxide of copper, are taken, and to one is added a solution of potash or soda; to the second, a solution of chloride of manganese; to the third, common water, taking care that the same volume of each fluid is added. The whole are now placed on a sand-bath, so as to be exposed to equal temperatures, and stirred occasionally. The suboxide of copper in the basin containing chloride of manganese oxidizes very rapidly; that in contact with the potash more slowly; and that with simple water is scarcely effected when both the others have lost their red colour. These actions are strictly in accordance with theory.

the suboxide being in a state of solution, because the soluble salts of the suboxide do not oxidize with such extraordinary ease, nor is it to be expected that they should, if we admit that the acid itself plays the part of oxygen. The accessory affinity of alkalies for oxygen is exhibited in many other cases of chemical action. Thus, colouring matters, such as deoxidized logwood, Brazil-wood, peach-wood, japan, fustic and catechu are oxidized more rapidly in contact with alkalies than in water alone ; and various dyeing principles, such as orcine and erythrine, absorb oxygen with great avidity in the presence of ammonia. Sugar may be boiled with potash without decomposition, but when air is admitted, formic, melassic, and glucic acids are produced. Hydruret of benzyle when exposed to air gradually absorbs oxygen and passes into benzoic acid, but in contact with potash this absorption is very much accelerated. The rapid decomposition of the gallates and of hematine in the presence of free alkali and air is a phænomenon of the same kind. In fact, numberless instances of this catalytic action of the alkalies are known to chemists.

We find the influence of an accessory oxidation in many cases of chemical union. Thus Campbell has shown \* that the transformation of cyanide of potassium into cyanate of potash is much accelerated by the presence of the iron in yellow prussiate of potash, the iron being converted into oxide during the transformation. Here the iron plays the part of the protoxide of manganese in the cases of oxidation already referred to, or it perhaps bears a more direct relation to the action of lead in communicating a tendency to the base metals to seize oxygen during the process of cupellation. The influence exerted by peroxide of manganese in first converting cyanide of potassium into cyanate of potash and afterwards into the carbonate of that base, is another instance of accessory affinity ; for only a portion of the oxygen is derived from the oxide employed. The solution of an alloy of silver and platinum in nitric acid may be supposed to be a similar affinity. It is not necessary to believe that this is a case proving the communication of intestine motion to the atoms of platinum, by which it acquires the power of decomposing nitric acid † ; for an equally simple explanation is given by assuming that the united affinities of platinum and silver are able to decompose nitric acid, both these affinities acting in one direction at the same time, and enabling the platinum to dissolve. We have only to suppose that the atoms of nitric acid are placed by the silver in a state of such tension that the platinum can

\* Phil. Mag. Third Series, vol. xix. p. 513.

† Liebig's Elements of Agriculture, 4th edit., p. 280.

now seize oxygen, which it could not do from the nitric acid when in a less tense state. The quartation of gold is obviously a phenomenon of the same kind. In these instances the interposing silver much reduces the cohesive or aggregative force of the platinum or gold, which opposes so strongly the action of nitric acid upon them. But when we have every atom of platinum or of gold separated by one of silver, great facility is given to the nitric acid to act upon these metals, especially when the silver at the same time aids them by its assistant affinity.

We have seen, in the consideration of the previous instances of catalysis, that the play of affinities was occasionally so nearly balanced, that a second disturbing cause determined the direction of the action. In the case of non-accendible phosphuretted hydrogen, the addition of another oxidizable body,  $\text{NO}_4$ , decided the union of oxygen with the gas. In accendible phosphuretted hydrogen the compound  $\text{PH}_2$  played the same part. When the accessory agent is present in small quantity, the preponderating affinity of the body acted upon shows itself in the result. But, as the action is due to two affinities nearly equal in amount, it is easy to conceive that the increased quantity of the accessory agent may exactly balance affinities, and that the catalytic phenomenon will be prevented. Thus one-twentieth of the volume of binoxide of nitrogen, according to Graham\*, added to accendible phosphuretted hydrogen, does not deprive it of inflammability, the bubbles of gas escaping into the air with a kind of explosion, although one-tenth volume of the same gas altogether prevents the accendibility. This nitric oxide, when pure, does not, like protoxide of nitrogen, render phosphuretted hydrogen spontaneously inflammable, the reason obviously being that its own affinity for oxygen is more powerful than that of the phosphuretted hydrogen. When added however in such small proportion to the accendible gas that the foreign constituent in it preponderates, then it becomes an accessory to the oxidation, though an increase of the quantity renders it more powerful, and prevents accendibility by itself seizing oxygen. Thus also larger volumes of gas, having an affinity for oxygen, but incapable like  $\text{NO}_4$  of gratifying that desire under ordinary circumstances, may exactly balance the feeble affinity of the foreign accessory body and prevent oxidation. Five volumes of hydrogen, 2 volumes of carbonic acid, 1 volume of olefiant gas, and 1 volume sulphuretted hydrogen, deprive 1 volume of phos-

\* Phil. Mag., Third Series, vol. v. p. 405.

phuretted hydrogen of its spontaneous inflammability\*. The very conception of a catalytic agent, on the view adopted, implies the exertion of an affinity, which is passed over or added to that of the body acted upon. If, therefore, a third body claim this added affinity, the increase of power being divided, may be insufficient to exert the force which it did when wholly applied to aid the affinity of one body. It may be this balancing of affinities which prevents the action of platinum on a mixture of oxygen and hydrogen. The platinum by its *surface affinity* condenses oxygen, and presenting it to hydrogen in a condensed form produces union. But in the presence of small quantities of certain oxidizable gases, such as sulphuretted hydrogen, carbonic oxide, and olefiant gases †, it ceases to exert this action, the assumption in this case being that the affinity of the added gases for oxygen balances that of hydrogen for the same gas.

This balancing of affinities may account for several phænomena otherwise inexplicable. On the decay of vegetable mould we find the hydrogen constantly diminishing in quantity until a certain period of decomposition, when the affinity of the carbon of the hunius for its hydrogen balances the affinity of the surrounding oxygen. It seems to be the same balancing of affinities which renders corrosive sublimate so antiseptic in its properties; but, in this case, the balance results from the affinity of the second atom of chlorine in the bichloride of mercury for the hydrogen of the organic substance, thus preventing its union with oxygen. It is probable that the same affinity of chlorine for hydrogen causes turpentine and the volatile oils to act catalytically in exploding chloride of nitrogen. The chlorine attracted by the hydrogen of these substances is drawn without the sphere of its attraction for nitrogen, and a disruption of the elements consequently ensues, compounds such as this resting on the very verge of separation between physical and chemical attraction. The antiseptic action of corrosive sublimate is very different from that exerted by sulphurous acid and sulphate of iron, these bodies acting by their superior affinity for oxygen, and neutralizing the power of the ferments or accessory oxidizers present in the organic body.

There is no difficulty in applying these notions of catalysis to organic compounds, which from the complexity of their

\* The influence which the vapours of turpentine exert in preventing the oxidation of phosphorus in the air is probably another instance of this balancing of affinities.

† Faraday, Phil. Mag., Third Series, vol. v. p. 405; Turner, Jameson's Journal, xi. 99 and 311.

molecules are peculiarly liable to change. If it once be admitted that an assisting affinity may exist in the sense defined in the present paper, then we see the same cause operating upon organic as well as inorganic molecules. When nitric acid acts on oxalic acid or starch, an inorganic body (a protosalt of manganese) lowers the temperature necessary for the oxidation, and exerts its influence until all the starch is converted into carbonic acid, being equally efficacious on the addition of more nitric acid and starch. Here the body acting as an assistant remains unchanged, and therefore continues its action *ad infinitum*, rendering it impossible to prepare oxalic acid from nitric acid and starch or sugar, carbonic acid being the only product\*. Had the assistant oxidizer passed from solution during the progress of the oxidation, it could not of course continue its favourable effect, and a new portion of it must have been added. Here the inorganic salt enables the sugar to oxidize itself from the surrounding medium just as yeast does, the only difference being that the yeast itself suffers change, and therefore can only continue its action for a limited period. It is exactly in the same condition as a mixture of nitric acid and binoxide of nitrogen made to act on protochloride of tin. A small portion of the latter added to such a mixture is oxidized, but when the solution is heated until all the  $\text{NO}_2$  is expelled, oxidation does not ensue on the addition of a new portion at the same low temperature as before. Now Saussure and Colin have shown that yeast only induces fermentation when it is in a position to absorb oxygen. It acts therefore strictly as binoxide of nitrogen, or a protosalt of manganese, in the previous instances, by adding its affinity for oxygen to that of the sugar, the added affinities of both completing the union. The only difference between these two decompositions is, that in one case the oxidizing agent is nitric acid, in the other it is water. The composition of sugar shows it to contain the elements of alcohol and carbonic acid *minus* an atom of water. In such a compound we have the affinity of carbon for hydrogen and of carbon for oxygen. The yeast by its nitrogen also exerts an affinity for hydrogen, and by its carbon for oxygen. The united affinities of the sugar and of the yeast acting upon water decompose it, its elements on their liberation being shared by the carbon of the sugar, for which it may be supposed to have the strongest affinities,  $\text{C}_{12} \text{H}_{11} \text{O}_{11}$ .

\* In this it resembles the action of oxalic acid in converting an unlimited quantity of oxamide into oxalate of ammonia, with this difference, that the oxalic acid, which causes the change, may not be the same, but a regenerated portion, while the salt of manganese always remains unchanged.

$+ \text{HO} = 4\text{CO}_2 + 2(\text{C}_4\text{H}_6\text{O}_2)$ . To show the exact similarity of the two processes of oxidation when the assisting body is either organic or inorganic, I may cite the curious manufacturing process for oxidizing oils in the method of dyeing Turkey-red used in this country, and included in Mercer's patent for that colour. It consists in oxidizing oils by blowing hot air through them, the oils being in contact with a solution of a salt of copper or of bran; the contact of either of these solutions is found very materially to accelerate the oxidation. The catalytic action of oxide of copper in evolving oxygen from hypochlorite of lime was adduced as showing its affinity for more oxygen, and this feeble affinity is well known and used empirically by all calico-printers, who are in the constant habit of mixing a salt of copper with their colours for the purpose of *ageing* them more speedily; in other words, of causing them to unite with oxygen. This also is the assisting cause in Mercer's process for oxidizing oils; bran in solution answers the same purpose from its affinity for oxygen. The addition of common salt or muriate of ammonia favours the oxidation in all the cases referred to, the oxidation proceeding much more quickly in their presence. No sub-chloride is ever formed, the action being purely catalytic, and probably depending on the conversion of the salt of copper into a chloride, the chlorine of which may be supposed to exert a slight affinity for the hydrogen of the compound, thus withdrawing it somewhat from the sphere of its own special attractions in the body; the copper now aiding the chlorine, delivers the hydrogen more easily into the power of the oxygen of the atmosphere. It is therefore immaterial whether the body exercising the assistant affinity be organic or inorganic, if the conditions be favourable to the exercise of this influence. The action of a body in acetous fermentation on the transformation of brandy into vinegar must be recognised as a phænomenon of a like kind. We know that brandy may trickle without change over a large surface of wood shavings, through which air circulates at the heat of the human body, but that it is quickly converted into vinegar if brandy in the act of oxidation be mixed with it. Here the added ferment exerts its assisting affinity in precisely the same way as the salt of copper, when it aids the oxidation of oils or colours, or as protonitrate of manganese or peroxide of nitrogen during the oxidation of starch. The conversion of hydrogen and oxygen into water by the action of fermenting silk, cotton, or woody fibre, as observed by Saussure, is obviously a phænomenon of the same kind, and can only be exerted slowly and in the immediate vicinity of the assisting oxid-

zers, just as a ball of spongy platinum silently effects the union of these two gases.

In these cases we must admit that the action is independent of a state of intestine motion of the atoms of one compound molecule imparted to those of another, or, if we do not allow this, we must create two new powers and separate decompositions caused by inorganic bodies from those produced by organic compounds, although all the phenomena of the decomposition show them to belong to one category.

In a body in a state of such incessant change as the blood of living animals, it would naturally be expected that an added agency, such as that described, would render it prone to abnormal actions and oxidations, and in fact we do recognise by all the recent progress in the study of public hygiene that the addition of any oxidizing miasm or putrid matter to the blood does produce those changes which are known by their results in the different forms of disease. These and other catalytic agents no doubt exercise most important influence on the processes of animal life and on the action of medicaments on the system, but it would be foreign to the object of this paper to examine them in detail.

The limits of a paper such as this compel me to avoid including many other instances of catalytic decompositions which come under this explanation, or of drawing special attention to those which cannot be included in the present state of our knowledge. Thus diastase, acting on starch, converts it into sugar, but we have so little knowledge of the composition or properties of the first body, that it would be unwarrantable to embrace a case such as this. But in analogous changes produced by bodies which are understood, the same power is recognised. Sulphuric acid in converting starch into grape-sugar offers an example of combination which may fairly be examined by the same method employed in investigating other decompositions. Graham has shown\* that heat is evolved even on the addition of the 48th atomic proportion of water to sulphuric acid, or, in other words, that the affinity of that acid for water is not gratified as long as our instruments of research can follow the change. This is merely another proof of the doctrine with which I started, that there is no evidence of such a complete gratification of affinity as ever to merge entirely the attractions of the elements of any body. In the case referred to, the development of heat on each successive addition proves that the water is condensed on entering into union with the acid. When the heat of the sulphuric acid is arti-

\* Phil. Mag. Third Series, vol. xxii. p. 334.

ficially increased, this compound is broken up, for distillation drives off the water and concentrates the acid. Now when starch is in the presence of this weak combination of sulphuric acid and water, at a temperature at which the latter is just able to exert its affinity and again have it destroyed by heat, it is not at all extravagant to suppose that the starch may seize the water in its nascent state at the moment of expulsion, or even that it may be able to unite with the last atoms of the series of acid and water when presented in that condensed state, although it cannot do so when the water is free and not nascent. Any such union would explain the transformation of starch into grape-sugar, the change merely being in the acquisition of water,  $C_{12}H_{10}O_{10} + 4HO = C_{12}H_{14}O_{14}$ . The action here is not the same, but the very reverse of that which ensues in the preparation of æther. In the one case the sulphuric acid abstracts water, in the other it is the means of adding it, and the difference of the action depends on the relative strength of the acids employed. Without at all giving an opinion in favour of the necessity for the formation of sulphovinic acid, as supposed by Liebig\*, or as to its not being an essential condition, as argued by Mitscherlich†, the final result is simply of the order now under consideration. In this decomposition the sulphuric or phosphoric acid is so strong that it combines with the water instead of yielding it, and the elevation of temperature essential to the change may either be due to the formation and after decomposition of sulphovinic acid, or it may be simply owing to the necessity of rendering the molecule of alcohol tense by heat, the elasticity of the æther and water both tending to break up the hydrate, the decomposition of which is determined by the presence of the strong acid now also aiding and abstracting the water. The final result is certainly purely catalytic in whatever light it is considered, although there may be more than one step in the process.

In conclusion, facts have been brought forward to show that there is at least as much probability in the view that the catalytic force is merely a modified form of chemical affinity exerted under peculiar conditions, as there is in ascribing it to an unknown power, or to the communication of an intestine motion to the atoms of a complex molecule. Numerous cases have been cited in which the action results when the assisting or catalytic body is not in a state of change, and attempts have been made to prove by new experiments that the catalytic body exercises its peculiar power *by acting in*

\* Geiger's *Pharmacie*, vol. ii. p. 711 *et seq.*

† *Lehrbuch der Chemie*, vol. i. p. 247 *et seq.*

*the same direction* as the body decomposing or entering into union, but under conditions in which its own affinity cannot always be gratified. The catalytic body is therefore a substance which acts by adding its own affinity to that of another body, or by exerting an attraction sufficient to effect decomposition under certain circumstances, without being powerful enough to overcome new conditions, such as elasticity and cohesion, which occasionally intervene and alter the expected result.

At the same time the theory is far from being fully proved; but if I have succeeded in rendering probable that the catalytic force is only chemical affinity recognised under an aspect which chemists have not been accustomed to view it, and exerted under conditions which can only be developed by close attention to details, it will not have been useless to direct increased study to this interesting class of phænomena.

**XXXVI. On Quaternions; or on a New System of Imaginaries in Algebra.** By Professor Sir WILLIAM ROWAN HAMILTON, LL.D., V.P.R.I.A., F.R.A.S., Corresponding Member of the Institute of France, and of other Scientific Societies in British and Foreign Countries, Andrews' Professor of Astronomy in the University of Dublin, and Royal Astronomer of Ireland.

[Continued from vol. xxx. p. 461.]

33. FOR the sake of those mathematical readers who are familiar with the method of co-ordinates, and not with the method of quaternions, the writer will here offer an investigation, by the former method, of that general property of the ellipsoid to which he was conducted by the latter method, and of which an account was given in a recent Number of this Magazine (for June 1847).

Let  $x y z$  denote, as usual, the three rectangular co-ordinates of a point, and let us introduce two real functions of these three co-ordinates, and of six arbitrary but real constants,  $l m n l' m' n'$ , which functions shall be denoted by  $u$  and  $v$ , and shall be determined by the two following relations:

$$u(l'l + mm' + nn') = l'x + m'y + n'z;$$

$$v^2(l'l + mm' + nn')^2 = (ly - mx)^2 + (mz - ny)^2 + (nx - lz)^2;$$

then the equation

$$u^2 + v^2 = 1 \dots \dots \dots \quad (1.)$$

will denote (as received principles suffice to show) that the curved surface which is the locus of the point  $x y z$  is an ellipsoid, having its centre at the origin of co-ordinates; and conversely this equation  $u^2 + v^2 = 1$  may represent any such ellip-

soid, by a suitable choice of the six real constants  $l m n l' m' n'$ . At the same time the equation

$$u^2 = 1$$

will represent a system of two parallel planes, which touch the ellipsoid at the extremities of the diameter denoted by the equation

$$v=0;$$

and this diameter will be the axis of revolution of a certain circumscribed cylinder, namely of the cylinder denoted by the equation

$$v^2 = 1;$$

the equation of the plane of the ellipse of contact, along which this circular cylinder envelopes the ellipsoid, being, in the same notation,

$$u=0:$$

all which may be inferred from ordinary principles, and agrees with what was remarked in the 29th article of this paper.

34. This being premised, let us next introduce three new constants,  $p, q, r$ , depending on the six former constants by the three relations

$$2p=l+l', \quad 2q=m+m', \quad 2r=n+n'.$$

We shall then have

$$l'x+m'y+n'z=2(px+qy+rz)-(lx+my+nz);$$

and the equation (1.) of the ellipsoid will become

$$\begin{aligned} & (ll'+mm'+nn')^2 \\ & = (l^2+m^2+n^2)(x^2+y^2+z^2) \\ & - 4(lx+my+nz)(px+qy+rz) \\ & + 4(px+qy+rz)^2 \\ & = (x^2+y^2+z^2)\{(l-x')^2+(m-y')^2+(n-z')^2\}, \end{aligned}$$

if we introduce three new variables,  $x', y', z'$ , depending on the three old variables  $x, y, z$ , or rather on their ratios, and on the three new constants  $p, q, r$ , by the conditions,

$$\frac{x'}{x} = \frac{y'}{y} = \frac{z'}{z} = \frac{2(px+qy+rz)}{x^2+y^2+z^2}.$$

These three last equations give, by elimination of the two ratios of  $x, y, z$ , the relation

$$x'^2+y'^2+z'^2=2(px'+qy'+rz');$$

the new variables  $x', y', z'$  are therefore co-ordinates of a new point, which has for its locus a certain spheric surface, passing through the centre of the ellipsoid; and the same new point

is evidently contained on the radius vector drawn from that centre of the ellipsoid to the point  $x' y' z'$ , or on that radius vector prolonged. We see, also, that the length of this radius vector of the ellipsoid, or the distance of the point  $x' y' z'$  from the origin of the co-ordinates, is inversely proportional to the distance of the new point  $x'' y'' z''$  of the spheric surface from the point  $l m n$ , which latter is a certain fixed point upon the surface of the ellipsoid. This result gives already an easy and elementary mode of generating the latter surface, which may however be reduced to a still greater degree of simplicity by continuing the analysis as follows.

35. Let the straight line which connects the two points  $x' y' z'$  and  $l m n$  be prolonged, if necessary, so as to cut the same spheric surface again in another point  $x'' y'' z''$ ; we shall then have the equation

$$x''^2 + y''^2 + z''^2 = 2(px'' + qy'' + rz''),$$

from which the new co-ordinates  $x'', y'', z''$  may be eliminated by substituting the expressions

$$x'' = l + t(x' - l), \quad y'' = m + t(y' - m), \quad z'' = n + t(z' - n);$$

and the root that is equal to unity is then to be rejected, in the resulting quadratic for  $t$ . Taking therefore for  $t$  the product of the roots of that quadratic, we find

$$t = \frac{l^2 + m^2 + n^2 - 2(lp + mq + nr)}{(x' - l)^2 + (y' - m)^2 + (z' - n)^2};$$

therefore also, by the last article,

$$t = \frac{x^2 + y^2 + z^2}{l^2 + m^2 + n^2 - 2(lp + mq + nr)};$$

consequently

$$t^2 = \frac{x^2 + y^2 + z^2}{(x' - l)^2 + (y' - m)^2 + (z' - n)^2};$$

and finally,

$$(x'' - l)^2 + (y'' - m)^2 + (z'' - n)^2 = x^2 + y^2 + z^2. \quad . \quad (2.)$$

Denoting by  $A$ ,  $B$ ,  $C$ , the three fixed points of which the co-ordinates are respectively  $(0, 0, 0)$ ,  $(l, m, n)$ ,  $(p, q, r)$ ; and by  $D$ ,  $D'$ ,  $E$ , the three variable points of which the co-ordinates are  $(x', y', z')$ ,  $(x'', y'', z'')$ ,  $(x, y, z)$ ;  $A B E D'$  may be regarded as a plane quadrilateral, of which the diagonals  $AE$  and  $BD'$  intersect each other in a point  $D$  on a fixed spheric surface, which has its centre at  $C$ , and passes through  $A$  and  $D'$ ; so that one side  $D'A$  of the quadrilateral, adjacent to the fixed side  $AB$ , is a chord of this fixed sphere. And the equation (2.) expresses that *the other side BE of the same plane quadrilateral, adjacent to the same fixed side AB, is a chord of a fixed ellipsoid*,

*if the two diagonals AE, BD' of the quadrilateral be equally long;* so that a general and characteristic property of the ellipsoid, sufficient for the construction of that surface, and for the investigation of all its properties, is included in the remarkably simple and eminently geometrical formula

$$\overline{AE} = \overline{BD'}; \dots \dots \dots \quad (3.)$$

the locus of the point E being an ellipsoid, which passes through B, and has its centre at A, when this condition is satisfied.

This formula (3.), which has already been printed in this Magazine as the equation (10.) of article 30 of this paper, may therefore be deduced, as above, from generally admitted principles, by the Cartesian method of co-ordinates; although it had not been known to geometers, so far as the present writer has hitherto been able to ascertain, until he was led to it, in the summer of 1846 \*, by an entirely different method; namely by applying his calculus of quaternions to the discussion of one of those new forms † for the equations of central surfaces of the second order, which he had communicated to the Royal Irish Academy in December 1845.

36. As an example (already alluded to in the 32nd article of this paper) of the *geometrical* employment of the formula (3.), or of the equality which it expresses as existing between the lengths of the two diagonals of a certain plane quadrilateral connected with that new construction of the ellipsoid to which the writer was thus led by quaternions, let us now propose to investigate geometrically, by the help of that equality of diagonals, the difference of the squares of the reciprocals of the greatest and least semi-diameters of any plane and diametral section of an ellipsoid (with three unequal axes). Conceive then that the ellipsoid, and the auxiliary sphere employed in the above-mentioned construction, are both cut by a plane AB'C', on which b' and c' are the orthogonal projections of the fixed points B and c; the auxiliary point d may thus be conceived to move on the circumference of a circle, which passes through a, and has its centre at c'; and since AE, being equal in length

\* See the Proceedings of the Royal Irish Academy.

† In reprinting one of those new forms, namely the following quaternion form of the equation of the ellipsoid:

$$(\alpha\varrho + \varrho\alpha)^2 - (\beta\varrho - \varrho\beta)^2 = 1,$$

a slight mistake of the press occurred at p. 459, vol. xxx. of this Magazine, which however, with the assistance there given by the context, can scarcely have embarrassed the reader. In the preceding page, for a hyperboloid of one sheet, touching the same cylinder in the same sheet, should have been printed, . . . in the same ellipse.

to  $BD'$  (because these are the two equal diagonals of the quadrilateral in the construction), must vary inversely as  $BD$  (by an elementary property of the sphere), we are to seek the difference of the squares of the extreme values of  $BD$ , or of  $B'D$ , because the square of the perpendicular  $BB'$  is constant for the section. But the longest and shortest straight lines,  $B'D_1$ ,  $B'D_2$ , which can thus be drawn to the auxiliary circle round  $C'$ , from the fixed point  $B'$  in its plane, are those drawn to the extremities of that diameter  $D_1C'D_2$  of this circle which passes through or tends towards  $B'$ ; so that the four points  $D_1C'D_2B'$  are on one straight line, and the difference of the squares of  $B'D_1$ ,  $B'D_2$  is equal to four times the rectangle under  $B'C'$  and  $C'D_1$ , or under  $B'C'$  and  $C'A$ . We see therefore that the shortest and longest semi-diameters  $AE_1$ ,  $AE_2$  of the diametral section of the ellipsoid, are perpendicular to each other, because (by the construction above-mentioned) they coincide in their directions respectively with the two supplementary chords  $AD_1$ ,  $AD_2$  of the section of the auxiliary sphere, and an angle in a semicircle is a right angle; and at the same time we see also that the difference of the squares of the reciprocals of these two rectangular semiaxes of a diametral section of the ellipsoid varies, in passing from one such section to another, proportionally to the rectangle under the projections,  $B'C'$  and  $C'A$ , of the two fixed lines  $BC$ ,  $CA$ , on the plane of the variable section. The difference of the squares of these reciprocals of the semi-axes of a section therefore varies (as indeed it is well-known to do) proportionally to the product of the sines of the inclinations of the plane of the section to two fixed diametral planes, which cut the ellipsoid in circles; and we see that the normals to these two latter or cyclic planes have precisely the directions of the sides  $BC$ ,  $CA$  of the *generating triangle*  $ABC$ , which has for its corners the three fixed points employed in the foregoing construction: so that the auxiliary and *diacentric sphere*, employed in the same construction, touches one of those two cyclic planes at the centre  $A$  of the ellipsoid. If we take, as we are allowed to do, the point  $B$  external to this sphere, then the distance  $BC$  of this external point  $B$  from the centre  $C$  of the sphere is (by the construction) the semisum of the greatest and least semiaxes of the ellipsoid, while the radius  $CA$  of the sphere is the semidifference of the same two semiaxes: and (by the same construction) these greatest and least semiaxes of the ellipsoid, or their prolongations, intersect the surface of the same diacentric sphere in points which are respectively situated on the finite straight line  $BC$  itself, and on the prolongation of that line. The remaining side  $AB$  of the same fixed or generating

triangle ABC is a semidiameter of the ellipsoid, drawn in the direction of the axis of one of the two circumscribed cylinders of revolution; a property which was mentioned in the 32nd article, and which may be seen to hold good, not only from the recent analysis conducted by the Cartesian method, but also and more simply from the geometrical consideration that the constant rectangle under the two straight lines BD and AE, in the construction, exceeds the double area of the triangle ABE, and therefore exceeds the rectangle under the fixed line AB and the perpendicular let fall thereon from the variable point E of the ellipsoid, except at the limit where the angle ADB is right; which last condition determines a circular locus for D, and an elliptic locus for E, namely that ellipse of contact along which a cylinder of revolution round AB envelopes the ellipsoid, and which here presents itself as a section of the cylinder by a plane. The radius of this cylinder is equal to the line BG, if G be the point of intersection, distinct from A, of the side AB of the generating triangle with the surface of the diacentric sphere; which line BG is also easily shown, on similar geometrical principles, as a consequence of the same construction, to be equal to the common radius of the two circular sections, or to the mean semiaxis of the ellipsoid, which is perpendicular to the greatest and the least. Hence also the side AB of the generating triangle is, in length, a fourth proportional to the three semiaxes, that is to the mean, the least, and the greatest, or to the mean, the greatest, and the least, of the three principal and rectangular semidiameters of the ellipsoid.

[To be continued.]

### XXXVII. Notices respecting New Books.

*Notice of a Memoir on Meteors of various sorts.* By T. I. M. FORSTER, F.R.A.S., &c. Bruges, 1846.

EXPERIENCED in observing and in treating of these phænomena, Dr. Forster refers his readers to his former communications of them, and to the numerous articles in the Royal Society's Transactions, as well as in the Gentleman's and Philosophical Magazines.

He carefully examines the theory of phosphorescent jets of gas rising unperceived while traversing the low and damp strata of the atmosphere, but becoming ignited as soon as they reach a sufficiently dry stratum. The ignition is then supposed to run down the column of gas, and reveal the several bends it had been subjected to by various currents of wind. The occasional explosions may be explained by supposing the running fire to reach a spot overbounding in hydrogen, instances not unfrequent after heavy rains.

It was not till the 10th of August 1811 that the idea of their periodicity occurred to Dr. Forster, when he and his father counted some hundreds, and by their journal perceived their recurrence on that same day. Indeed, in copying a curious old manuscript calendar, he found the 10th and 18th of August called *stellibundaæ* and *meterodes*; but he acknowledges their frequency at all times and in all places.

Inclined to assign them a gaseous origin, our author has yet, in deference to the learned men who differed from him, endeavoured to relate fairly the various arguments in favour of their several theories.

*Aristotle* regarded meteors as arising from exhalations denoting an approaching change of weather. *Theophrastus* thought they prognosticated wind from the quarter towards which they rushed. And *Aratus* agreed with him, especially if they left long lingering tails, in which he was imitated by *Virgil*. *Lucan* in his *Pharsalia* rather confounds meteors with the fixed stars. *Homer* compares the descent of Minerva to the rush of a meteor.

Passing over the middle ages, when meteors were feared as indications of Divine anger, we find that in the seventeenth century electricity began to be suspected, and was supported by the highest names of that era. Then the magnificent meteor of the 18th of August 1783 brought out the elaborate paper by Dr. Blagden in the Philosophical Transactions for the following year. As to their velocity, it varies so much that this element cannot suffice to decide from what height they fall. The meteor above alluded to moved at only six miles per second when at about ninety miles above our heads. Cavallo estimated its diameter at 3200 feet, and its elevation at 560 miles. Certainly the explosion not being heard for ten minutes after it was seen is a sufficient proof of its distance. The general electric state of the atmosphere that year over half the globe is well known, by the remarks made in consequence of the violent earthquakes that occurred.

In support of the theory that meteors are occasioned by the ignition of columns of inflammable gas, Dr. Forster mentions the *ignis fatuus*, and the flitting lights that are seen in May on cabbages. Many naturalists regard meteors as one of the various phænomena attributable to electricity, and some expected to find that they chiefly pointed to the magnetic pole.

Many roofs of thatch have been ignited by the fall of meteors upon them, and this must be the explanation of towns recorded to have been burnt by fire from heaven. The explosion of the meteor of the 25th of September 1846, was heard *a few* seconds after it was seen: but if, instead of the ambiguous term *a few*, spectators would count slowly, they would afford a much nearer approach to the true time elapsed, especially if they would afterwards count at the same rate when they can compare with a seconds watch, or with a clock. (A.S.) The tail of that meteor was larger than usual, and lasted longer, some persons stating fifty seconds, others some minutes. More precise details are requisite. It was at first whitish, then purplish, and lastly red, when it became curved, and faded in a serpentine

form. This last phænomenon was observed in another instance about twenty years since. Even the luminous arc of the 28th of September 1828 might, our author thinks, be a still more dilatory tail of a meteor that had shot across our hemisphere just before sunset, and for that reason was not perceived. In July 1799 Dr. Forster's father saw a meteor cross the sky from south to north, then return southward, and finally bend to the north-west. Another peculiarity is that of rising in the sky instead of descending, which has been reported as occurring sometimes near the equator, where they are very numerous. And Dr. Forster himself saw a whitish globe stationary for two seconds, and then turn a fine red.

A shower of small meteors is recorded to have occurred on the 25th of April 1095 ; and Dr. Forster saw an approximation to this on a bright winter night in 1832, inasmuch as the whole firmament was in a glow from an immense number of very fine luminous tails nearly parallel from E.N.E. to W.S.W. They might deserve the name rather of streaks, no heads being visible. The duration of each might not exceed a second, but the phænomenon altogether lasted a quarter of an hour and then ceased suddenly. And in November 1830 he saw a similar multiplicity of little streaks, but crossed by others at right angles. Another peculiarity was described by a clergyman near Epping, that of seeing a meteor, after descending to the earth, undergo a sort of reverberation by rising in an oblique direction, and then break into sparks.

Among the numerous authors who have treated of this subject, perhaps M. Quetelet's catalogue is the most complete, with the exception of his omitting the interesting meteor of 1783. M. Arago and M. Biot have also treated the subject ably.

A copious journal of meteors has been kept in Dr. Forster's family from 1767, but no periodicity was suspected till the 10th of August 1811 ; though then, on looking back through the journal, it was perceived that there had been a great preponderance in the Novembers ever since 1799, and in the Augests from 1779. When employed a few years after to construct perennial calendars, Dr. Forster indicated a number of meteors as a phænomenon to be expected on the 10th of August.

This became confirmed in 1831 by other observers, and they added the second period of the 13th of November. M. Quetelet now adds April and December, while others suggest January, May, June and July. He thinks their usual height in the atmosphere is from sixteen to twenty leagues or more, though they are occasionally seen slanting very near the ground. The most numerous sort, distinguished by the name of *étoiles filantes*, may revolve in trajectories by swarms, forming a belt round the sun, which we have occasionally to traverse. Then, owing to the earth's motion, these luminous corpuscles would naturally, as they have been observed to do, appear to "have their point of divergence towards  $\beta$  Camelop. in August, and towards  $v$  Leonis in November, agreeing with our annual motion in the ecliptic." According to the known laws of optics, the swarm would seem to separate in radii as we neared them, and,

owing to the compound velocities, seem to tend from N.E. to S.W.

Although meteors differ very much from each other in some instances, it is very difficult to classify them; but an abundance of them seems connected with a change of weather, and especially with cirrostratus and cirrocumulus clouds. As to their direction, though they sometimes converge towards one point, they rush at others towards every point of the compass. He therefore wavers only between an electric and a gaseous origin,—quoting electric experiments referred to in England by the Abbé Bertholon, and gaseous ones by Constable, as having produced excellent imitations.

In the terrible night of the 7th of July 1834, a crowd of nimbi collected around Vesuvius about 9 o'clock, shooting their lightnings down towards the mountain accompanied by rain and hail. The lightning was sometimes bluish and sometimes reddish.

As to the periodicity of meteors, Dr. Forster finds that there are decided changes in the electrometers also on the 10th of August and 13th of November; and the greatest number he ever saw fell on the 10th of August 1811, just after a violent storm; but when a storm has happened some time before, the meteors are fewer at the two periods observed. Also if one or more large meteors occur, there are no small ones afterwards for a proportionate time, as if the atmosphere had been cleared of the requisite material. Also it may be remarked in general, that the winter and the higher latitudes are least prolific of them.

Fiery balls do not often occur, but are very powerful. Thus the one seen in France and in England the 17th of July 1771, must have been at an elevation of fifty-four miles, and the report of its explosion was not heard till two minutes after its occurrence, like the rolling of thunder; but the observatory windows at Paris were "*ébranlées*." It appeared larger and brighter than the  $\odot$ , and its swiftness was estimated at twenty-four miles per second.

From the quickly-increasing rarity of our atmosphere, Arbuthnot thinks that at the height of sixty miles (the estimated height of the meteor in 1718) the air is 30,000 times purer than on the level of the sea. Yet Pringle estimated the height of the meteor of 1738 to have been ninety miles. The diameter of some globes has been estimated at  $1\frac{1}{2}$  mile.

### XXXVIII. *Proceedings of Learned Societies.*

#### ROYAL SOCIETY.

[Continued from p. 77.]

June 17, "RESEARCHES on the Function of the Intercostal Muscles and on the Respiratory Movements, with some remarks on Muscular Power, in Man." By John Hutchinson, M.R.C.S. Communicated by Sir Benjamin Brodie, Bart., F.R.S., &c.

The object of this paper is to demonstrate by models and dissections the action of the intercostal muscles.

After premising an account of the views of several eminent physiologists, and in particular those promulgated by Haller, the author shows that they resolve themselves into the general opinion that the scalene or other muscles of the neck fix the first rib, in order to enable the two sets of intercostal muscles to act either separately or conjointly, as inspiratory or expiratory muscles. - He then proceeds to state the proofs that the intercostal muscles possess an action which is independent of any other muscle, and also independent of each other, so that any of the twelve ribs may be elevated or depressed by them either separately or conjointly. He demonstrates the nature of this action by means of models, producing oblique tensions between levers representing the ribs, and allowing of rotation on their centres of motion; and he shows that such tension in the direction of the external intercostal muscles, elevates both the levers until the tension ceases, or the position of the bars by proximity obstruct each other. If the tension be exerted in a contrary direction, as in the internal intercostal muscles, the bars are both depressed. This movement was demonstrated by a model. It was farther shown that two tensions decussating can, according to the position of the fulera, be made to act as associates or antagonists to each other. Such motions are to be considered with reference to the fulera, bars with one fulcrum common to each having no such action; and the author accordingly draws the following conclusions:—

1st. All the external intercostal muscles are true inspiratory muscles, elevators of the ribs, and with this act they dilate the intercostal spaces, thus increasing the cavity of the chest.

2nd. The internal intercostal muscles have a double action; the portions situated between the cartilages are associates in action with the external layer, and act as elevators of the cartilages, while the portion between the ribs are depressors, or antagonists of the external layer, and are here true expiratory muscles; with this they decrease the intercostal spaces.

3rd. These muscles can elevate or depress the ribs independently of any other muscle, fixing the first or last rib. Any one lamella, or series of muscles, can, as required, independently perform inspiration or expiration at any one of the twenty-two intercostal spaces.

4th. In inspiration, the intercostal spaces increase, with a shortening of the muscle; and in expiration, they decrease their perpendicular distance, with a shortening of the muscle.

5th. All parallel intercostal muscles, acting with uniform force, concur in the same effect, whether near the fulcrum or more distant from it, and these muscles gain power with their increasing obliquity as well as speed.

In the third part of the paper an account is given of the difference between the external thoracic space and the internal pulmonic space. The respiratory movements are described in health and disease, and it is shown that the chest is rarely enlarged at two places at one and the same time.

In conclusion the author conceives that he has established the following propositions:—

1st. Costal breathing may be distinguished from abdominal by determining which part is first put in motion, and the kind of respiration may be designated according to the name of such part.

2nd. Healthy costal breathing begins with the motion of a superior rib, which is followed by that of the lower ones in succession.

3rd. Ordinary respiration in men is abdominal, in women, costal; extraordinary breathing is the same in both sexes.

4th. Any of the ribs, from the twelfth to the first, may carry on respiration.

5th. Diseased respiration is of various kinds; the movements may be symmetric or not symmetric, costal or abdominal; all or none of the ribs may move; the abdomen may or may not move; the chest may dilate in all its dimensions at one and the same time; costal and abdominal breathing may alternate with one another; costal motion may be undulating or not; and all these may be combined in one, which the author terms "*hesitating breathing*"; and lastly, the quantity of air breathed is diminished when there exists pulmonary disease.

"On the Structure and Development of the Liver." By C. Handfield Jones, M.B., Cantab. Communicated by Sir Benjamin C. Brodie, Bart., F.R.S., &c.

The author gives a detailed description of the structure of the liver in animals belonging to various classes of the animal kingdom. He states that in the Bryozoon, a highly organized polype, it is clearly of the follicular type; and that in the Asterias, the function of the liver is probably shared between the closed appendage of the stomach and the terminal cæca of the large ramifying prolongations of the digestive sac contained in the several rays. Among the Annulosa, the earthworm presents an arrangement of the elements of the hepatic organ, corresponding in simplicity with the general configuration of the body, a single layer of large biliary cells being applied as a kind of coating over the greater part of the intestinal canal. In another member of the same class, the Leech, in which the digestive cavity is much less simple, and presents a number of sacculi on each side, these elements have a very different disposition; and the secreting cells, although some remain isolated, for the most part coalesce to form tubes, having a succession of dilatations and constrictions, and finally uniting and opening into the intestine. In Insects, the usual arrangement is that of long curved filamentary tubes, which wind about the intestine; these, in the meat fly, are sacculated throughout the greater part of their course, till they arrive quite close to the pylorus, where they open; near their origin they appear to consist of separate vesicles, which become gradually fused together, but occasionally they are seen quite separate. The basement membrane of the tubes is strongly marked, and encloses a large quantity of granular matter of a yellowish tinge, with secreting cells; another portion of the liver consists of separate cells lying in a granular blastema, which cells, in a later stage

of development, are seen to be included in vesicles or short tubes of homogeneous membrane, often coalescing and exhibiting a more or less manifestly plexiform arrangement; this portion of the liver is regarded by Mr. Newport as really adipose tissue. The author has termed it the *Parenchymatous portion* of the liver, on account of its general appearance and mode of development, though he has not been able to determine whether the tubes always originate from it. Among the Arachnida, the follicular type of arrangement prevails; and the same is the case with the Crustacea, the follicles in these last being distinctly visible to the naked eye. In Mollusca also, we find the follicular arrangement universally to obtain; yet in certain cases the limiting membrane of the follicles cannot be shown to exist, and the author therefore thinks that its importance is probably not great, but that it serves chiefly to fulfil the mechanical function which its synonym "*basement*" indicates. The quantity of retained secretion in the liver of molluscs seems clearly to imply that the bile in them is not an excrementitious fluid; it is used slowly on account of the imperfect character of the respiration.

In passing from the Invertebrata to the Vertebrate division of the animal kingdom, and beginning with the class of Fishes, a great change is immediately manifest in the form and character of the biliary organ; it is now a gland of solid texture, to which the term *parenchymal* is justly applied. Two portions may be distinguished in it, namely, the secreting parenchyma, consisting of delicate cells, or very often of nuclei, granular and elaborated matters in great part, and the excreting ducts, which, though completely obscured by the surrounding bulky parenchyma, may yet be satisfactorily demonstrated, and traced often to their terminal extremities in the following manner. If a branch of the hepatic duct be taken up in the forceps, it may be dissected out without much difficulty from the surrounding substance, which is very soft and yields readily to gentle manipulation; when a trunk is in this way removed and placed under the microscope, a multitude of minute ramifications are seen adhering to it; among these not a few may be discovered, which do not appear to have suffered injury; some are occasionally seen terminating by distinctly closed extremities; more usually the duct becomes very minute and gradually loses all definite structure, appearing at last like a mere tract of granular matter; in either case there is no communication by continuity with the surrounding parenchyma. Large yellow corpuscles, peculiar cells, and a considerable quantity of free oily matter usually existing in the liver of various fishes, seem generally to indicate a great superiority in the amount of secretory over that of excretory action, and to betoken clearly the feeble intensity of the aërating function.

In Reptiles, there is the same arrangement in the liver, namely, a secreting parenchyma of cells and an apparatus of excretory ducts, which have the same essential characters as those of fishes; but there exists very frequently in the parenchyma remarkable dark corpuscles, which appear to be masses of retained biliary matter,

the import of which, in the situation they occupy, is doubtless the same as that of the similar masses existing in fishes.

In Birds, the parenchyma of the liver is remarkably free from oily or retained biliary matters; it often consists almost wholly of free nuclei and granular matter, with scarcely a single perfect cell; the excretory ducts often greatly resemble those of reptiles, sometimes rather those of mammalia; the essential character is, however, always the same, namely, that they terminate without forming any important connexion with the parenchyma.

In Mammalia, the parenchyma of the liver consists usually of perfect cells, which are arranged often in linear series of considerable length, radiating from the axis of each lobule; these unite at various points with each other, so as to present a more or less decidedly plexiform appearance. Each lobule, as described by Mr. Kiernan, is separated from the adjacent ones by the terminal twigs of the portal vein, and to a greater or less extent by a "fissure," though in most animals the lobules are continuous with each other both above and below the fissure. The elaboration of the secreted product seems to be most completely effected in the cells adjoining the margins of the lobules, which are often seen to contain a larger quantity of biliary matter than those in the interior, and to be apparently in the act of discharging it into the fissure; the margin of the lobule then presents an irregular surface with large globules of the secretion clustering together all over it. The capsule of Glisson surrounding the vessels in the portal canals gives a fibrous investment to those surfaces of the lobules which are towards the canal; but when it has arrived in the fissures, it forms a continuous membrane lining the surfaces of opposite lobules; this membrane is often truly homogeneous, and closely resembles the basement tissue: there appears occasionally to be a delicate epithelium on its free surface; but this, as well as the membrane itself, is often absent, when the margin of the lobules is in that condition which has just been described and which may be termed *active*. The minute branches of the hepatic duct as they approach their termination undergo a remarkable alteration in their structure; they lose their fibrous coat, which blends itself with the membranous expansions of the capsule of Glisson; their basement membrane becomes gradually indistinct, and at last ceases to exist, and the epithelial particles no longer retain their individuality, but appear to be reduced to mere nuclei, set very close together in a faintly granular basis substance. The mode of their termination is not uniformly the same; frequently they present distinctly closed rounded extremities, between one and two thousandths of an inch in diameter; at other times they seem to cease gradually in the midst of fibrous tissue, the nuclei alone being disposed for some little way in such a manner as to convey the idea of a continuation of the duct. These ducts can seldom be discerned in the fissures, but have several times been seen in the "spaces," where several fissures unite; they do not form anything like a plexus between the lobules. From the anatomical relation of the ducts to the parenchyma, and from the circumstance that a

distinct vessel conveying a different kind of blood is distributed to the hepatic duct, as soon as the liver assumes the parenchymal form, it seems probable that the mode in which the secreted bile is conveyed out of the organ, is by its permeating the coats of the minute ducts in obedience to an endosmotic attraction, which takes place between the bile in which the ducts may be said to be bathed, and a denser (perhaps mucous) fluid formed in their interior. The large quantity of oily matter frequently existing in a free state in the secreting parenchyma of the liver, which must be regarded as a product of secretory action, seems to suggest the idea, that a certain quantity of the biliary secretion may be directly absorbed into the blood, and in this manner conveyed away from the organs, just as occurs in the thyroid body, suprarenal capsules, and other glands unprovided with efferent ducts.

With respect to the development of the liver, the author considers the opinion of Reichart to be decidedly the correct one, namely, that its formation commences by a cellular growth from the germinal membrane, independently of any protrusion of the intestinal canal. On the morning of the fifth day, the cesophagus and stomach are clearly discernible, the liver lying between the heart, which is in front, and the stomach which is behind; it is manifestly a parenchymal mass, and its border is quite distinct and separate from the digestive canal; at this period, the vitelline duct is wide, it does not open into the abdominal cavity, but its canal is continued into an anterior and posterior division, which are tubes of homogeneous membrane, filled, like the duct, with opaque oily contents; the anterior one runs forwards, and forms behind the liver a terminal expanded cavity, from which then passes one offset, which, gradually dilating, opens into the stomach; a second, which runs in a direction upwards and backwards, and forms apparently a caecal prolongation; and a third and fourth, which are of smaller size, arise from the anterior part of the cavity and run to the liver, though they cannot be seen to ramify in its substance; at a somewhat later period, these offsets waste away, excepting the one which is continued into the stomach, and then the mass of the liver is completely free and unconnected with any part of the intestine. As the vitelline duct contracts, the anterior and posterior prolongations of it become fairly continuous and form a loop of intestine, the posterior division being evidently destined to form the cloaca and lower part of the canal. The final development of the hepatic duct takes place about the ninth day by a growth proceeding from the liver itself, and consisting of exactly similar material; this growth extends towards the lower part of the loop of duodenum, which is now distinct, and appears to blend with the coats of the intestine; around it, at its lower part, the structure of the pancreas is seen to be in process of formation. The further progress of development of the hepatic duct will, the author thinks, require to be carefully examined, but the details he has given in this paper have satisfied him of the correctness of the statement that the structure of the liver is essentially parenchymal.

### XXXIX. *Intelligence and Miscellaneous Articles.*

#### SUGGESTIONS FOR THE OBSERVATION OF THE ANNULEAR ECLIPSE, OCT. 9, 1847, MADE BY THE BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE, OXFORD, JUNE 26, 1847.

THE following directions and suggestions, relative to the ensuing annular eclipse of the sun, which will take place Oct. 9, 1847, are proposed for the assistance of less-practised observers, or those who may not have better information at hand, but who may nevertheless render great service by noticing and recording, as well as circumstances permit, any of the various points herein alluded to.

I. As a general direction as to the limits within which the eclipse can be seen annular in England and Ireland, if on any map a line be drawn through Greenwich and Gloucester and produced, it will give the northern limit at which the eclipse ceases to be annular.

A line parallel to the last, through Padstow in Cornwall on the west, and Torbay on the east (which will extend across the channel to Havre, &c., and passes just below Cape Clear on the west), will be the line along which the eclipse is both annular and *central*.

The southern limit lies wholly below England.

II. As a rough guide to the *time*, the commencement of the annulus will be nearly at 7<sup>h</sup> 23<sup>m</sup> A.M. (civil reckoning) for the extreme south-west of Ireland, at 7<sup>h</sup> 24<sup>m</sup> for a line through Land's End and Milford Haven, at 7<sup>h</sup> 25<sup>m</sup> through the Isle of Wight and Reading, at 7<sup>h</sup> 25<sup>m</sup> 50<sup>s</sup> for Walmer (Greenwich mean time).

III. For the observations requisite, a telescope of very moderate power is best. As the annulus will not last more than three or four minutes, those unaccustomed to such observations should be cautioned against attempting to observe *all* the phænomena, or they may thus run the risk of observing *none*. If possible several observers should combine for the purpose, and *each* agree to attend to *one*, or *some few* of the phænomena.

IV. To obviate some of the difficulties arising from the rapid passage of the phænomenon, the observer may be referred to Capt. Smyth's Cycle (i. 141, 146), where some valuable practical hints are thrown out for tranquillizing the observer's nerves in so transitory a phænomenon; especially by previously making a careful drawing of the spots (if any) existing on the sun's disc, which may be made useful in marking and ascertaining the progress of the eclipse.

V. With the view of correcting the moon's tabular north polar distance and semidiameter, it is peculiarly desirable that observations should be made along or near the line (passing through Greenwich and Gloucester) on which the eclipse is barely annular. At some of these the eclipse will be completely annular, and here the following observations should be made:—

The time of beginning of annularity and end of annularity should be observed. As the duration only is required, a common watch showing seconds will suffice for this purpose.

If possible, by means of a graduated pearl scale or other equivalent means, the breadth of the narrowest part of the annulus should be measured several times about the middle of the time of the annular appearance, as well as it can be estimated.

At other places the eclipse will not be completely annular, and here the principal object must be to make several measures of the distance between the cusps about the time when that distance is smallest. This measure may probably be made by means of a graduated pearl scale, or by means of a divided object-glass applied in front of the object-glass of the telescope, or by the use of a common sextant.

VI. As to the particular points of physical interest to which attention should be directed, they may be stated as follows:—

1. It will be desirable in general to notice *the fact* of the appearance of what are denominated "beads" and "threads" by the late Mr. Baily and others, just before and after the completion of the annulus.

For details of older observations the observer should consult

Ast. Soc. Memoirs, i. 142–146, x. 10–17, 33–38.

The beads were observed by Mr. Baily, ib. x. 210, in 1842, when they were not seen by Mr. Airy, ib. x. 218.

They were observed by Prof. Henderson at Edinburgh. Ast. Soc. Notices, v. 186.

2. Whether in the neighbourhood of the cusp the limb either of the sun or moon appears distorted?

Whether the beads appear *steady* or waving, disappearing and reappearing, &c.?

See the observations of Mr. Caldecott at Trevandrum, Ast. Soc. Notices, vi. 81.

Whether they present any peculiar changes when viewed through differently coloured glasses, the observer alternating the colours, which should be as dissimilar as possible, such as red and green?

See Silliman's Journal, Jan. 1842.

3. Whether they are seen when the eclipse is projected on a *screen*?

In this way Prof. Chevallier saw none when others with coloured glasses saw them. Ast. Soc. Notices, v. 186.

4. The drawing out of the beads into *threads* when very near junction; and whether they *waver* and *change*, and the number of them?

See Ast. Soc. Mem., x. 15–17, 39; waving and changing, ib. x. 12, 13; not seen in 1842 by Mr. Baily, Notices, v. 210.

5. Whether before and after the formation of the threads the moon's dark disc is *elongated* towards the point of contact?

This was observed, ib. x. 29; and wavy motion in the limb, ib. x. 12, 14, 30.

6. The beads are ascribed by some to *lunar mountains*: What mountains exist at that part of the limb?

See Ast. Soc. Mem., x. 9, 16, 30–36.

7. The exact intervals of time elapsed between the first and last complete contact, and that of the first and last formation of beads or other irregularities in or about the cusps, should be determined. The difference of the times being all that is wanted, a good ordinary watch will be sufficient.

The remarkable fact of a *recurrence* of cusps observed by Mr. Airy in 1842, and his explanation of it, should be attentively considered. See *Ast. Soc. Notices*, v. 296.

8. If possible, accurate *measures* should be taken of the *apparent diameter* of the dark disc of the moon upon the sun, which may be expected to be greatly less than the truth, owing to the irradiation of the sun's light.

9. It should be noticed whether any external *luminous arch* is formed over the part between the cusps, a little before the first junction and after the final separation, and the *colour* of the light.

It was observed, and appeared *brown* to De Lisle (*Phil. Trans.*, 1748, 490), *reddish* in other cases (*Ast. Soc. Mem.*, i. 144, x. 37), and *purple* in others (*ib. x. 16*).

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#### ON THE PREPARATION AND COMPOSITION OF THE SALTS OF ANTIMONY. BY M. E. PELIGOT.

*Sulphates of Antimony.*—When oxychloride of antimony ( $\text{ClSb}^2\text{O}^2$ ) is treated with hot concentrated sulphuric acid, a salt is formed which is deposited in acicular crystals, hydrochloric acid being at the same time evolved. This salt, as well as another sulphate to be described, can only be obtained in a dry state by long remaining *in vacuo*, or in perfectly dry air upon porous plates of pipe clay. These plates were heated to redness before the crystalline magma was placed upon them, and they were left to cool in air deprived of moisture. This method of drying yields products which usually contain a slight excess of sulphuric acid. If however the points of contact between the salt to be dried and the absorbent earth be renewed from time to time, and the absorption goes on for several months, compounds of sufficient purity to remove all doubts of their true composition may be obtained.

One hundred parts of the sulphate of antimony, obtained by common sulphuric acid and oxychloride of antimony, gave—

Sulphuric acid .....	51·9
Oxide of antimony (by carbonate of ammonia) .....	50·2

The composition of this salt is therefore—

4SO <sub>3</sub> .....	2000	51·2
Sb <sup>2</sup> O <sub>3</sub> .....	1912	48·8
	3912	100·0

Another specimen gave 53·1 of sulphuric acid, and 44·3 of oxide of antimony.

Another sulphate of antimony was obtained in the form of small brilliant crystals, by treating sesquioxide of antimony with Nordhausen sulphuric acid. After remaining ten months on the dried clay, it gave—

Sesquioxide of antimony ....	63·0	64·3
Sulphuric acid .....	37·1	35·0

The formula  $2\text{SO}_3 \cdot \text{Sb}^2\text{O}_3$  gives 65·6 oxide of antimony and 34·4 sulphuric acid.

Mixtures of these salts in different proportions were also obtained;

but no analysis indicated the existence of the compound  $3\text{SO}^3$ ,  $5\text{Sb}^2\text{O}^3$ , which, according to Berzelius, would be the neutral sulphate of antimony.

On treating the above-described salts with hot water, a subsalt is obtained, the composition of which is represented by the formula—

	Calculation.	Experiments.
$2\text{Sb}^2\text{O}^3$ . . . . .	3824	88·4
$\text{SO}^3$ . . . . .	500	11·6
	<hr/> 4324	<hr/> 100·0
		100·0

The analysis of two other specimens is correctly represented by the formula  $2\text{Sb}^2\text{O}^3$ ,  $\text{SO}^3$ ,  $2\text{HO}$ .

*Nitrate of Antimony.*—This salt was obtained in the form of pearly crystals by dissolving the oxide in cold fuming nitric acid, and adding water to the solution. Its composition is  $2\text{Sb}^2\text{O}^3$ ,  $\text{NO}^5$ .

*Oxychlorides of Antimony.*—Powder of Algaroth was prepared by treating chloride of antimony with cold water. After some days the mass became crystalline; when well-washed its composition agreed with the analyses which have served to fix the formula of this compound. This formula is more simply replaced by  $\text{Cl Sb}^2\text{O}^2$ .

When the sesquichloride of antimony, or rather the sesquioxide dissolved in a great excess of hydrochloric acid, is treated with hot water, another oxychloride is obtained, which, on the cooling of the liquor, precipitates in dense brilliant crystals. Its composition is represented by the following formula:—

	Calculation.	Experiments.
$\text{Cl}$ . . . . .	443	10·6
$4\text{Sb}$ . . . . .	3224	77·3
$\text{O}^5$ . . . . .	500	12·1
	<hr/> 4167	<hr/> 100·0

This compound consequently must be presented by the formula,  $\text{Cl Sb}^2\text{O}^2 + \text{Sb}^2\text{O}^3$ .

*Tartrates of Antimony.*—By allowing a syrupy solution of tartrate of antimony, obtained by dissolving the oxide of the metal in tartaric acid, to remain for a long time, large transparent crystals of tartrate of antimony were obtained. The mother-water, after the separation of the crystals, furnished more afterwards by spontaneous evaporation.

This salt is very soluble in water. It is deliquescent in a moist atmosphere. Its composition is represented by the following formula:—

	Calculation.	Experiments.
$\text{C}^{16}$ . . . . .	1200	19·6
$\text{H}^{16}$ . . . . .	200	3·2
$\text{O}^{28}$ . . . . .	2800	46·0
$\text{Sb}^2\text{O}^3$ . . . . .	1912	31·2
	<hr/> 6112	<hr/> 100·0

At  $320^\circ$  F. this salt lost 23·1 per cent. of water.

On decomposing the formula as follows, the loss of twelve equivalents of water represents 22 per cent. of the weight of the salt—



On pouring alcohol into a concentrated solution of the acidulous tartrate of antimony, a precipitate is obtained which, when dried at  $320^{\circ}$  F., yielded 16·4 of carbon and 1·3 of hydrogen. The composition of this salt is represented by the formula  $\text{C}^8\text{H}^2\text{O}^8, \text{Sb}^2\text{O}^3, \text{HO}$ , which requires 17·2 of carbon and 1 of hydrogen. The salt which M. Peligot analysed contained a little more water than the quantity required by this formula, but not enough to allow of the addition of another equivalent.

*Acidulous Tartrate of Antimony and Potash.*—This salt was described by M. Knapp, who obtained it by mixing solutions of tartaric acid and tartarized antimony. The salt which was analysed by M. Peligot was in very regular crystals. It yielded—

Carbon .....	19·5	18·7
Hydrogen .....	2·7	2·7
Sesquioxide of antimony ..	31·0	

The formula  $\text{C}^{16}\text{H}^4\text{O}^{16}, \text{Sb}^2\text{O}^3, \text{KO}, 8\text{HO}$  represents its composition. It gives—

Carbon .....	19·1
Hydrogen .....	2·3
Sesquioxide of antimony ..	30·5

According to M. Knapp it contains one equivalent less of water.

*Oxalate of Antimony.*—M. Peligot prepared this salt by four processes:—1st, by boiling in a solution of oxalic acid oxide of antimony prepared from the chloride by carbonate of ammonia; 2nd, by treating the powder of Algaroth with oxalic acid; 3rd, by pouring hydrochloric acid into a hot solution of the double oxalate of potash and antimony; the oxalate of antimony precipitates in the state of a crystalline powder; 4th, by adding oxalic acid to a solution of the same double salt.

The oxalates of antimony obtained by these processes are similar in composition. The author attempted, but in vain, by varying the proportions, to obtain other compounds of oxalic acid and oxide of antimony. This salt is crystalline and insoluble in water. It is decomposed by boiling water into oxalic acid, which dissolves, and sesquioxide of antimony.

Its composition is represented by the following formula:—

	Calculated.		Experiments.		
$\text{C}^4$ .....	300·0	10·2	10·1	10·6	10·6
$\text{O}^6$ .....	600·0	20·6			
$\text{Sb}^2\text{O}^3$ ....	1912·9	65·4	66·7	65·6	
$\text{HO}$ .....	112·5	3·8	3·8	4·5	4·0
	<hr/> 2925·4	<hr/> 100·0			

*Double Oxalate of Potash and Antimony.*—The preparation and analysis of this salt are very difficult. The salt obtained by M. Pe-

ligot was crystallized in transparent prisms ; it is readily soluble, and is decomposed by a large quantity of water.

The quantity of water in this salt appeared to vary from unknown causes, but apparently dependent on the temperature at which the salt crystallizes. The formula appeared to be  $7\text{C}^2\text{O}^3$ ,  $\text{Sb}^2\text{O}^3$ ,  $3\text{KO}$ ,  $6\text{HO}$ . This gives as the composition of 100 parts of the salt—

Carbon .....	13·9
Water .....	9·0
Oxide of antimony .....	25·7
Potash .....	23·5

M. Peligot obtained—

Carbon.....	13·7	14·3	14·4	14·0
Water .....	9·7	9·2	10·1	8·9
Oxide of antimony .....	25·7	26·2	24·8	

*Ann. de Ch. et de Phys.*, Juillet 1847.

#### ACTION OF HYDROCHLORIC ACID IN THE FORMATION OF OXALIC ACID.

M. Kopp states that the presence of hydrochloric acid in nitric acid is peculiarly favourable to the formation of oxalic acid. The resins of benzoin and Tolu, treated with pure nitric acid, yield no oxalic acid ; but with an impure acid it is obtained. Pure nitric acid occasions the formation of terebic acid only, in acting upon oil of turpentine, and to oxypicric acid, in oxidizing the gum-resins. By using nitric acid containing much hydrochloric acid, oxalic acid only is obtained under the same circumstances.—*Ibid*, Juillet 1847.

#### PROJECTION OF ALDEBARAN ON THE MOON.

At the British Association in Oxford a question arose respecting the apparent projection of Aldebaran on the disc of the moon in occultations. Prof. Airy and Dr. Forster stated having seen this phænomenon, which Prof. Struve seemed disposed to attribute to some mal-adjustment of the telescopes. On looking back, however, to the Philosophical Magazine, it will be found that this appearance has been three or four times recorded ; as well as some other circumstances calculated to show that the light of different stars is very differently refracted. See Phil. Mag. for April and May 1824.

#### THE PUFF PARLIAMENTARY :—DISINFECTION.

The art of puffing has not yet exhausted its resources ; and a Parliamentary Report well got up, printed at the expense of the public, and from which extracts may go the round of the newspapers, seems to be the last and boldest device for the purpose, which however has been fearfully exposed in the Dublin Quarterly Journal of Medical Science.

The Times newspaper in a leading article of the 20th of August, felicitates itself on having “the pleasant task of giving what publicity it may to a discovery made by a French gentleman, M. Ledoyen,

a Parisian chemist, in concert, it would appear, with a Mr. F. C. Calvert, who seems to have received his education as a chemist at Paris, and who is now lecturer at the Royal Institution of Manchester. This discovery, which, under the auspices of Lord Morpeth, has been submitted to the most searching tests by Dr. Southwood Smith, Mr. Toynbee and Mr. Grainger, promises fair to be *one of the greatest boons ever conferred on suffering humanity*. The discovery is nothing less than the means of disinfecting all foetid animal substances and gases by a liquid which is very cheap, simple, and can be applied by any person with the greatest facility.

"The three medical gentlemen appointed by Lord Morpeth to inquire into the real value of M. Ledoyen's discovery, present us in their report with a dismal catalogue of the offensive and dangerous vapours from animal and vegetable substances which at all hours infect the air we breathe, in a greater or less degree, accordingly as we more or less neglect their impure origins." "The Commissioners state that they have tried the effect of this fluid,—1, on substances already in a state of decomposition; 2, on substances undergoing that process; 3, on night soil; 4, on impure air. In every instance excepting the second these experiments have been attended with the *most miraculous result*." "It would almost seem that *some mysterious power* had sent us M. Ledoyen and his discovery to compensate for the shortcomings of the Premier and Lord Morpeth\*."

So far The Times.—We now give a few extracts from the Dublin Journal, and refer our readers to the article which it contains for the details of the means by which these puffs have been procured, and for a full account of the matter.

This boasted discovery professes to furnish "the means of disinfecting all foetid animal substances and gases by a liquid which is very cheap, simple, and can be applied by any person with the greatest facility. It disinfects night-soil, not destroying but increasing vegetation, more particularly as regards agriculture, completely preventing the disease in potatoes when the land is manured with disinfected night-soil. It disinfects hospital-wards of miasma; also cellars, water-closets, and buildings infected by impure gases. It disinfects sailors suffering from fever on board of vessels; it will also disinfect ships at sea, and under quarantine. It disinfects patients suffering with infectious disorders and wounds, also dead bodies, so that they may be kept nearly a month; also different parts of the body can be kept for the purposes of dissection, for coroners' inquests, &c."

\* No wonder that competitors should have started up asserting their claims to so wonderful a discovery. Mr. W. Maddick thus begins his letter to the Editor of the Times; of whose judgement in matters of science he seems to have a most exalted opinion:

"Sir,—All the world knows that a laudatory notice in your columns is a very high honour; and as in your excellent leader of yesterday you have highly eulogized Messrs. Ledoyen and Calvert for their alleged discovery, I appeal with confidence to the proverbial justice of The Times, &c. &c.

"I boldly claim originality in this matter, and challenge these gentlemen, or any other," &c., &c.

"There is not a word of evidence in the document before us as to the influence of this solution of nitrate of lead in curing, or 'disinfecting,' as they call it, by its vicinity, fever or other infectious diseases. Of course no professional man (except Dr. Southwood Smith) could bring himself to support such an absurdity as that would amount to. With respect to the potatoe disease, Dr. Smith has been even less guarded. He manured portions of his garden with his disinfected night-soil, and finds that potatoes grown on these spots are finer than elsewhere. He says, 'I have this day had specimens of them examined by Mr. Alfred Smee, who pronounces them to be at present perfectly healthy.' What! not a single *Aphis vastator*! Oh, genius of humbug! how numerous are thy votaries! Truly, successful speculation constitutes the idolatry of this age, and the wonder-workings of pseudo-science its superstition."

"Let us now briefly pass in review some of the evidence detailed in this precious document—some of the 'Letters and Reports received by the Chief Commissioner of Woods and Forests,'—set forward in a parliamentary folio, gravely ordered to be printed by the British senate, and consequently paid for by the country. Always premising that we do not deny to this, in common with many other chemical substances\*, the power of destroying some unpleasant odours, or, to deal more in the phraseology of the Report, *stinks*. But against the disgraceful quackery with which this book abounds,—a quackery not equalled by the most offensive and indecent advertisement,—and the humbug of presenting such a book to the country, we loudly and strongly protest."

"We have already alluded to the circumstance that this imposture has been attempted to be bolstered up by the testimony of night-men, dissecting-room porters, ward-men, and other respectable authorities of a similar kind. Some of the experiments made by these intellectual and educated individuals may amuse our readers, as they have doubtless enlivened the House of Commons. Speaking of the contents of a privy—

"William Fenwick did, as you gentlemen saw, *taste* it, and William Dyer put some over his eyes without injuring them: if it had not gone through your process, it would have *blinded* him!!'

"We cannot however pursue a strain of levity when we come to examine the part which a physician of repute has taken in this transaction. Dr. Southwood Smith, not content with bearing his share in the fooleries of the Report already spoken of, volunteers his individual testimony as to the efficacy of the fluid in obviating contagion among the medical and non-medical attendants on the sick.

"Whatever difficulties,' he writes, 'your Lordship may have encountered in obtaining the necessary powers to make even any com-

\* Sulphate of copper, nitrate of copper, chloride of copper, super-nitrate of bismuth, nitrate of lead, nitrate of silver, chloride of gold, protochloride of tin, perchloride of tin, nitrate of mercury. This fluid has been examined by Dr. Aldridge, and found to be a solution of nitrate of lead. Sir W. Burnett has introduced the chloride of zinc for similar purposes in the navy.

mencement of a system of prevention by the removal of the causes of fever, you have in your own hands, and have had for some months, the sure and certain means of preventing the extension of fever to the immediate attendants on the sick.'

"In the columns of newspapers, in the pages of journals, on the covers of magazines, in the corners of railway guides, placarded on dead walls and bankrupts' shop-windows, dropped into the hat at public meetings, thrust into the hand in streets, and forced upon the attention at every turn, we thought all the modes of puffing quack advertisements and indecent labels, either in prose or rhyme, had been exhausted: but we find that we were mistaken. A novelty in this department has been introduced by Colonel Calvert; and in the pages of a parliamentary report\* we see puffs as gross, and language as indelicate, as any that disfigure the lowest newspapers."

We can only add an expression of our regret that an important public cause, that of sanitary improvements, should have to encounter prejudices raised against it from the exaggerations, misrepresentations, quackery, and jobbing which are too manifest in the conduct of some of its advocates.

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#### A GRANT OF 200*l.* TO MR. WILLIAM STURGEON.

We are glad to learn, from a communication dated Downing Street, 12th August, from Colonel Grey, the private secretary of Lord John Russell, that his Lordship has been pleased to grant the sum of 200*l.*, from the Royal Bounty Fund, to Mr. William Sturgeon of this town. Mr. Sturgeon was formerly lecturer on experimental philosophy at the Hon. East India Company's Military Academy, Addiscombe; and since his residence in Manchester, now extending over a number of years, he has been superintendent of the Victoria Gallery, delivering various courses of lectures there; and subsequently he filled the office of lecturer to the Manchester Institute of Natural and Experimental Science. For a long series of years Mr. Sturgeon has honourably distinguished himself by his investigations and discoveries in the various branches of electrical science, especially in electro-magnetism and thermo-electricity.

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#### OBSERVATIONS ON CREATINE. BY M. HEINTZ.

About two years ago I described a peculiar substance which I had discovered in the normal urine of man. From subsequent investigations I find that this substance is identical with that which M. Chevreul found in meat broth, to which he gave the name of creatine, and the presence of which in the fresh muscular flesh of different animals has recently been shown by Liebig.

The most advantageous method of procuring the substance is that subsequently pointed out by M. Pettenkofer; it consists in adding

\* That Parliamentary Reports are sometimes made vehicles of privileged detraction and calumny the public are already aware. A late instance with regard to the Greenwich Observatory has been exposed by the Astronomer Royal.

to the alcoholic extract of the urine an alcoholic solution of chloride of zinc; in a short time a deposit is formed, which contains the creatine in combination with the chloride of zinc, together with a small quantity of phosphate of zinc. These two substances are separated by boiling water, which dissolves the first, but is without action upon the latter. The pure creatine is obtained from the aqueous solution of its combination with chloride of zinc by precipitating the zinc with hydrosulphate of ammonia; after having evaporated the filtered liquid as far as possible without a precipitate being formed in the boiling solution, absolute alcohol is added to it, when the creatine is immediately deposited in the form of small crystals, resembling those obtained in operating upon the alcoholic solution of the aqueous extract of meat.

After having washed these crystals with alcohol, I recrystallized them from water. The elementary analysis of the pure crystals led to the following formula,  $C^8 H^9 N^3 O^4 + 2HO$ , which is the same as that advanced by M. Liebig.

When creatine enters into combination with chloride of zinc, it parts with 2 atoms of water besides the water of crystallization, and in exchange takes up 1 atom of this salt. This combination is represented by the following formula,  $C^8 H^7 N^3 O^2 + ClZn$ , and the atomic weight of creatine is consequently 1412·5.

From the experiments of M. Liebig it results, that of all the organs of the animal body it is only the muscles which yield creatine. Now, as I have proved its presence in the urine of man and animals, it appears placed beyond all doubt that this substance is formed in the muscles, that it is absorbed by the lymphatics or blood-vessels, and is finally secreted by the kidneys, like urea, &c. We may therefore conclude that creatine should henceforth be placed amongst the *excrementitious* substances; and consequently it is barely probable that it constitutes one of the most important alimentary principles of meat broth, as M. Liebig is inclined to think. Is it not rather one of the ultimate products of the chemical actions, the presence of which we have great reason to suspect in the act of muscular contraction?—*Comptes Rendus*, March 22, 1847.

#### THE NEW PLANET IRIS.

The following letter to The Times appeared on Wednesday, Aug. 18th.

SIR,—In addition to the Berlin maps, which we have revised, and in some instances corrected, ecliptical charts of stars down to the tenth magnitude have been formed for some of the hours of right ascension, which it is Mr. Bishop's intention to publish as soon as they are completed. On the 13th of August I compared Wolfer's map with the heavens, and was surprised to find an unmarked star of 8·9 magnitude in a position which was examined on June 22 and July 31 without any note being made. The mere existence of a star in a position where before there was none visible, would not have been sufficient to satisfy me as to its nature; because during an eight months' search I have met with very many variable stars,—a

class which I believe to be far more numerous than is generally supposed. But, on employing the wire micrometer we were enabled in less than half an hour to establish its motion, and thus to convince ourselves that I had been fortunate enough to discover a new member of the planetary system. It may appear to many of your readers rather bold to announce the existence of a new planet from the detection of so small an amount of motion as 2 s. 5 in. R.A.; but such is the firm mounting of the large refracting telescope, and the perfection of the micrometers (for which we have to thank Mr. Dollond), that a far smaller change would have been sufficient to convince us as to the nature of the object in question. Mr. Bishop has fixed upon Iris as an appropriate name for the new planet; and we hope that astronomers generally will join with us in its adoption. The following are all the observations we have yet made:—

	G. M. T. h. m. s.	R.A. of Iris. h. m. s.
Aug. 13,	9 39 46	19 57 30·38
— 13,	10 37 24	19 57 28·41
— 14,	9 23 58	19 56 38·30
— 15,	9 0 39	19 55 47·64

I remain, Sir, your most obedient Servant,  
 Mr. Bishop's Observatory, Regent's Park, J. R. HIND.  
 Aug. 17.

We have been favoured with the following additional information by Mr. Hind:—

The planet was observed by Mr. Rümker at Hamburg, on Aug. 20, and by Prof. Gauss at Göttingen and Prof. Encke at Berlin, on Aug. 21. M. Leverrier announced the discovery to the Paris Academy of Sciences on Aug. 16, giving at the same time a general view of the various hypotheses which have been started respecting the group of small planets. The orbit of Iris appears to be very excentrical, and the period longer than that of any other asteroid; but further observations are required for the accurate determination of the elements.

Prof. Schumacher's "Planeten-Circular" was despatched from Altona on August 20, so that we may expect a general series of meridian observations at the various European observatories during the present apparition of the planet.

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#### SUGGESTIONS FOR PROMOTING THE SCIENCE OF METEOROLOGY.

*To the Editors of the Philosophical Magazine and Journal.*

GENTLEMEN,

As I find the Meteorological Society is defunct, I beg leave to suggest that in order that the science of meteorology may be improved and promoted, and not left to chance, and in order that uniformity in the observations may be obtained, I propose that at the several railway stations, the head clerk, or the cleverest man on the premises, be supplied gratis with proper instruments, and that these instruments should all be supplied by the same maker; then will they all start fair, upon certain data, which by the present system cannot be done. And as my friend Mr. Luke Howard has suggested to

me, would not the electric telegraph be a capital means of transmitting the intelligence of a thunder or hailstorm, or any change that has taken place in any part of the kingdom where railways obtain, and by that means unravel nature's secret with regard to meteorological phenomena?

But as those stations should be provided with every requisite for taking all the necessary observations, so as to form a compendious series of meteorological remarks, you will ask who is to furnish the means? In answer to that I would say, could not the Royal Society do that, and might not the British Association take the concern under their fostering care? You will also say, would not the attention necessary to be paid to these observations lead to inattention in respect to the trains? I hope not; and I believe, before long, such improvements will be made in railways as to make it nearly a physical impossibility for accidents to occur.

Boston, July 3, 1847.

SAMUEL VEALL.

#### METEOROLOGICAL OBSERVATIONS FOR JULY 1847.

*Chiswick*.—July 1. Light clouds: fine: overcast. 2. Slight drizzle: cloudy. 3. Overcast: clear. 4. Very fine: clear: cloudy. 5. Sultry. 6. Very fine. 7. Overcast: slight shower. 8. Rain: cloudy: clear. 9. Cloudy and fine. 10. Overcast: clear. 11, 12. Very fine. 13. Sultry. 14—16. Excessively hot. 17. Thunder, lightning and heavy rain all the morning: fine: cloudy. 18. Cloudy. 19. Slight showers. 20. Overcast and fine. 21. Very fine. 22. Heavy clouds: clear at night. 23, 24. Very fine. 25. Overcast. 26. Clear and fine. 27, 28. Very fine. 29. Sultry. 30, 31. Very fine.

Mean temperature of the month .....  $65^{\circ}84$

Mean temperature of July 1846 .....  $65^{\circ}46$

Mean temperature of July for the last twenty years .....  $63^{\circ}08$

Average amount of rain in July ..... 2·36 inches.

*Boston*.—July 1—3. Cloudy. 4, 5. Fine. 6. Fine: half-past 2 P.M. thermometer  $76^{\circ}$ . 7. Fine: rain early this morning. 8. Cloudy: tremendous storm of thunder, lightning and rain P.M. 9. Fine. 10, 11. Cloudy. 12. Fine: 4 P.M. thermometer  $81^{\circ}$ . 13. Fine. 14. Cloudy. 15. Cloudy: 3 P.M. thermometer  $74^{\circ}$ . 16, 17. Cloudy. 18—21. Fine. 22. Rain. 23. Cloudy. 24—27. Fine. 28, 29. Cloudy. 30, 31. Fine.

*Sandwick Manse, Orkney*.—July 1. Cloudy. 2, 3. Fog: fine. 4. Damp: cloudy. 5. Cloudy: fog. 6. Fog. 7. Drops. 8. Rain: clear. 9. Bright: fine. 10. Fog: bright: fine. 11. Bright: fine. 12. Clear: fine. 13. Damp: cloudy. 14. Bright: showers. 15. Clear: fine. 16. Bright: fine. 17. Cloudy. 18. Rain. 19. Drizzle: damp. 20. Drizzle: cloudy. 21. Drizzle: fog. 22. Showers: rain. 23. Cloudy: showers. 24. Cloudy: fine. 25. Fine. 26. Bright: drizzle. 27. Rain: cloudy. 28. Showers. 29. Showers: clear. 30. Bright: showers. 31. Bright: rain.

*Applegarth Manse, Dumfries-shire*.—July 1. Very fine: thunder. 2—4. Very fine. 5. Very fine: mackerel sky and sultry P.M. 6. Very fine. 7, 8. Heavy showers: thunder. 9. Cloudy and threatening. 10. Rain. 11. Rain: fog P.M. 12. Fine, but cloudy. 13. Very fine: fog early A.M. 14. Heavy dew: very fine. 15. Very fine: shower and thunder. 16. Cool and breezy: thunder. 17. Very fine: air elastic. 18. Very fine: drizzle P.M. 19, 20. Very fine. 21. Fine, but cloudy: shower and thunder. 22. Showers: refreshing. 23. Fair and fine. 24. Fair and fine, but dull. 25. Shower early A.M.: fine. 26. Fine bracing air. 27. Cloudy: threatening: thunder. 28. Fair, but cloudy. 29—31. Fair, but cloudy: unsettled.

Mean temperature of the month .....  $61^{\circ}55$

Mean temperature of July 1846 .....  $59^{\circ}20$

Mean temperature of July for twenty-five years .....  $58^{\circ}14$

Average rain for twenty years ..... 3·91 inches.

*Meteorological Observations made by Mr. Thompson at the Garden of the Horticultural Society at Chiswick, near London; by Mr. Veall, at Boston; by the Rev. W. Dunbar, at Applegarth Manse, DUMFRIES-SHIRE; and by the Rev. C. Clouston, at Sandwick Manse, ORKNEY.*

THE  
LONDON, EDINBURGH AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
AND  
JOURNAL OF SCIENCE.

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[THIRD SERIES.]

OCTOBER 1847.

XL. *Fourth Memoir on Induction. By M. ELIE WARTMANN, Professor of Natural Philosophy in the Academy of Geneva\**.

[With a Plate.]

[Continued from vol. xxx. p. 272.]

§ XIV. *On the Commutators employed to render voltaic currents discontinuous, and to separate currents of induction.*

116. IT is exactly a century since a remedy for various ailments was first sought in the electric fluid. The first experiments were made at Geneva by Prof. Jallabert in 1747†. At a later period, when the voltaic battery was invented, its physiological effects were studied, and they are now employed for the cure of various affections, such as obstinate ulcers‡, dumbness§, deafness||, blindness¶, tic-doloureux\*\*, paralysis††, &c. Lastly, since the discovery of magnetic and electric induction in 1831 by Mr. Faraday, it has been found that the induced currents, as well as the electrical discharges of the Leyden jar, have an extremely short duration, and produce greater shocks than batteries of a large number of elements. The idea therefore has occurred of rendering the current of the electromotor apparatus discontinuous, to approximate it

\* Communicated by the Author.

† *Expériences sur l'Electricité*, p. 127. 8vo. Geneva, 1748.

‡ Bocquerel, *Traité de Physique*, vol. ii. p. 638. Paris, 1844.

§ Namias, *De alcuni effetti dell'elettrico sopra l'Animale Economia, &c.*, p. 27. Venice, 1841.

|| *Giornale per servire ai progressi della Patologia et della Terapeutica*. Gennajo, 1843, p. 108. *Giornale delle Scienze Mediche di Torino*, vol. iv. p. 430.

¶ *Giornale per servire, &c.*, December 1841, p. 658. *Biblioteca Italiana*, fascicolo 25, p. 12, &c.

\*\* Zantedeschi, *Trattato della Elettricità*, vol. ii. p. 525.

†† *Giornale di Fisica, &c. di Pavia*, decade II. vol. vii. p. 284; and vol. viii. p. 219. *Annali delle Scienze del Regno Lombardo-Veneto*, January and February 1833, &c.

to the cases of induced currents. Dr. Neeff of Frankfort on the Maine, in 1835\*, and M. Masson in the following year †, have made very conclusive experiments on this subject. An instrument described by M. Poggendorff under the name of *inversor* ‡, is intended to render the current of an ordinary battery at the same time discontinuous and in an alternate direction through a given conductor.

117. At the present day the employment of induced currents seems to become more and more general. In place of the original magnets employed in the apparatus of Ritchie §, Pohl ||, Pixii ¶, Saxton \*\*, Clarke ††, Störer ‡‡, and others, a simple voltaic pair has been substituted, and an instrument has been constructed, of small size, easy of transport, and producing almost unlimited effects, called an *electro-electric machine*, or a *shock-machine*. M. Bonijol constructs this machine with such perfection that it has been generally adopted, and there is at the present day scarcely an hospital where it is not found. It is employed in the treatment of a multitude of nervous affections; in that of amaurosis §§, in assisting parturition ||||, and as a diagnostic to ascertain the state of vitality of the foetus.

118. I have had more than one opportunity of convincing myself that many persons make use of the shock-machine without understanding either its construction or its theory. This machine, arranged on a different plan, might be rendered both more intelligible in its mode of action and more useful to the physicist and the physiologist. I will point out some of the cases in which it may be employed, and afterwards the arrangement applicable to each of them.

119. A voltaic current being given, it may be proposed—

1. To render it discontinuous, without changing its direction, in a conductor  $\alpha$ ;

\* *Das Blitzrad, ein Apparat zu rasch abwechselnden galvanischen Schließungen und Trennungen.* Pogg. Ann., vol. xxxvi. p. 352, and vol. xlvi. p. 104.

† *Comptes Rendus de l'Acad. des Sciences de Paris*, vol. iv. p. 456.

‡ Pogg. Ann., vol. xlvi. p. 372 and 385. § Phil. Trans., Oct. 1833.

|| Pogg. Ann., vol. xxxiv. p. 185 and 500.

¶ Ann. de Ch. et de Phys., vol. I. p. 322.

\*\* Phil. Mag. N. S. vol. ix. p. 360. †† Ibid. p. 262.

‡‡ Pogg. Ann., vol. lxi. p. 417, 1844.

§§ Cunier, Dr., *Annales d'Oculistique*, vol. xii. and vol. xvi., where will be found a memoir by Dr. Hæring On the Employment of the Electro-magnetic rotatory apparatus in Diseases of the Eyes.

|||| See on this subject, P. Kerz, *De electro-magnetismi vi et usu in arte obstetricia*. Bonn, 1846.—J. A. Schmidt Müller, *Handbuch der medizinischen Geburtshilfe*.—T. Radford, Galvanism applied to the treatment of uterine Hæmorrhage. Manchester.—Von Kilian, *Die Geburtslehre von Seiten der Wissenschaft und Kunst*.—*Neue zeitschrift für Geburtkunde*, von H. Bursh, d'Outrepont, &c., vol. xvi. No. 26, &c.

2. To render it discontinuous, and in alternately contrary directions.

This current being employed to react on a wire B, near the conductor A, it may be required—

3. To isolate the direct currents, induced from the closing of the circuit A;

4. To isolate the inverted currents, induced on breaking this circuit;

5. To emit these currents successively, giving them the same direction;

6. To emit them alternately in contrary directions, just as they are produced directly.

It is known that there is a reaction of the induced currents on the principal current. We may therefore desire—

7. To collect the totality of their reaction;

8. To avail ourselves only of the reaction of the direct induced currents;

9. To avail ourselves only of that of the inverted induced currents;

10. To collect only the induction of the inductor on itself.

120. Physicists have studied the majority of these cases; but the mechanical instruments which they have imagined and described under the names of *disjuncteur*\*, *tachytrope*†, *rheotrope*‡, *gyrotrope*§, or *commutator*||, are scarcely applicable except to one or other of the first two categories. The most complete of these instruments, reinvented in Paris seven years after having been described and employed in Germany, is composed of four isolated wheels on the same axis, the outline of which presents successively metallic and ivory arcs, against which press conducting springs. The axis is set in motion by means of a handle or tooth-wheel. Sometimes the interval of the teeth is left void, and the spring in escaping determines the opening of the circuit. Other commutators are formed with needles arranged on isolated axes, in such a manner that one is immersed in mercury at the instant when the other

\* Dove, *Magneto-elektrischer Apparat zum Hervorbringen inducirter Ströme gleicher Intensität in von einander vollkommen getrennten Drähten*. Pogg. Ann., vol. xlivi. p. 511. 1838.

† Dove, *Ueber den Gegenstrom zu Anfang und Ende eines primären*. Pogg. Ann., vol. lvi. p. 251.

‡ Masson et Breguet, *Mémoire sur l'induction*. Ann. de Ch. et de Phys., vol. iv. p. 134. 1842.

§ Pogg. Ann., vol. xxxii. p. 539; and vol. xxxiv. p. 185 and 500. 1834-35.

|| Jacobi, *Sur l'application de l'Electro-magnetisme au mouvement des machines*, § VII. Potsdam, 1835. Taylor's Scientific Memoirs, vol. i. p. 503. Archives de l'Electr., vol. iii. p. 244.

comes out of it\*. These different systems are complicated, and subject to several inconveniences. The rheotrope, which I shall proceed to describe, and which is especially applicable to electro-electric machines, combines with the advantage of

\* On the 18th of June, 1840, I communicated to the Society of Physics and Natural History of Geneva an apparatus of this kind, the construction of which presents no difficulty, and which is deposited in the Cabinet of Physics in the Academy of Lausanne. The following is a description of it:—  
“ My commutator is composed of a pure copper stem *a b* (Plate II. fig. 1), intersected in the middle by a piece of ivory *c*: the latter is hollowed into the nut of a screw, in such a manner that the two halves of the stem screw into it. Between these metallic extremities some sealing-wax is run, in order to isolate them entirely. The cylinder thus formed is arranged horizontally, and each of its branches is furnished with symmetrical pieces at equal distances. These pieces are two copper teeth *e f*, placed perpendicularly and at a right angle on the axis; then a copper circle *g*. Lastly, to one of the extremities of the stem is fixed a pulley *h*, in the groove of which there runs a cord *i*, which again passes over a lower pulley *k*, which is much larger, vertical, and moveable by means of the handle *m* in one of the supports of the apparatus.

“ The six projecting pieces of copper dip into a glass vessel *n* (fig. 2), placed on two small horizontal bars *o*; it presents six isolated compartments full of mercury. The extreme circles remain immersed in this liquid during the entire rotation of the stem, the arrangement of the teeth causing one to be immersed whilst the neighbouring one is not. It is easy to regulate the quantity of mercury in the troughs so that the immersion of the one may correspond exactly to the exit of the other.

“ Supposing it be desired to emit into a rheometer the two induced currents, giving to them the same direction, it is sufficient to bring the extremities of the wire in which the induction is produced in the extreme compartments reserved for copper circles. The ends of the wire of the multiplicator are tied to bars of copper connecting the troughs *e f*, *e f*, corresponding on the right and left of the isolator *c* to the needles fixed at a right angle. So likewise on connecting the extremities of the rheometric wire only with the troughs *f f*, or with the troughs *e e*, it is evident that the direct or inverted induced currents only may be collected.

“ I have combined with this arrangement one which M. Bonijol has employed in some of his apparatus. It consists (fig. 3) of planting one of the ends of the stem in a flattened wooden cylinder *r*, on which a spring *s* presses, passing into a circular cylinder *t* of hard wood, and the free extremity of which *u* is placed by the rotation of *r* in contact with an amalgamated metallic capsule *x*, or is removed from it. Then, by connecting the spring on one side, and the capsule on the other, with the wire which the direct current of the pile traverses, we obtain by the simple rotation of the stem any number of inductions.

“ This apparatus enabled me to discover that the thermo-electric currents are capable of induction like the hydro-electric currents. I employ a single bismuth-antimony pair, the solder of which is kept at  $100^{\circ}$  by steam. The bismuth extremity is connected with the spring *s*, the antimony extremity with a wire covered with silk, which makes seventy turns on a frame, and terminates at the capsule *x*. On the same frame is rolled an isolated and finer copper wire which makes 1200 coils (110.), and both ends of which terminate in the troughs *p q*. The induced circuit is closed by a very delicate rheometer (5 *a*), which deviates five degrees and more,

being more simple, and consequently less subject to derangement, that of not requiring the employment of mercury, and of serving to solve all the cases above stated.

121. H (Plate II. fig. 4) is a reel on which two *insulated* wires are wound; one the inductor A, by which the current of the battery  $p\ n$  is made to pass; the other the induced B, intended to become the seat of the currents of induction. *Three* brass wheels  $r, s, t$ , of the same diameter, are isolated from one another on a common axis; their circumference presents an equal number of parts alternately of metal and wood. Two metallic springs  $a, b$  are fixed against the wheel  $r$ , in such a manner that the first leans against a conducting arc, and the other against an insulating arc. The wheels  $s$  and  $t$  are each pressed by two springs  $c\ d, e\ f$ , similarly arranged. The central metallic parts of the three wheels are in constant communication with the springs  $g, h, i$ .

122. If it be desired to collect the voltaic current always in the same direction after having rendered it discontinuous, it is sufficient to connect the spring  $i$  with the pole  $p$  by a wire  $\alpha$ , and the other pole  $n$  with the spring  $f$ , by means of any conducting wire different from the wires A and B wound upon the reel. If it is wanted to obtain, as with the *inversor*, the discontinuous current in directions alternately contrary, we must join the springs  $c$  and  $e$  as well as the springs  $d$  and  $f$ , and then connect the extremity of the conjunctive wire of the battery with the spring  $h$ .

123. When it is desired to employ currents of induction, the contact of the extremity  $l$  of the inducting wire with the pole  $n$  is established permanently, and that of the extremity  $m$  with the spring  $f$ . Now, to isolate the direct currents induced at the closing of the circuit A, we have only to connect the ends  $x$  and  $y$  of the wire B respectively with the springs  $b$  and  $g$ .—To isolate the inverted currents, we unite  $x$  with  $h$  and  $y$  with  $d$ .—To cause the direct and the inverted currents to pass one after another in the same direction through the rheometer G, for example, we connect the springs  $a$  and  $c$  with the end  $s$  of the wire of the instrument, the springs  $b$  and  $d$  with the end  $t$ , the extremity  $x$  with the spring  $h$ , and the extremity  $y$  with the spring  $g$ .—To collect the induced currents alternately in contrary directions, just as they are produced directly,

when it is traversed by direct and inverted currents in the same direction." (See the Transactions of the Helvetic Society of Natural Sciences for 1840, pp. 173, 195.)

Prof. Dove has demonstrated thermo-electric induction by a different process. His researches were made at the same time as mine, and in an independent manner. (See Pogg. Ann., vol. xlix. p. 97. 1840.)

we disconnect the extremities  $x$  and  $y$  of the wire B from the springs of the rheotrope.

124. Lastly, if we propose to employ the reaction of the induced wire B on the inductor A, and that of the inductor wound in a helix on itself, we substitute for the wire  $\alpha$  the body which is to be subjected to the effects of these reactions. We then employ one of the four arrangements above described (123.), according as we wish to obtain the totality of influence of the two currents induced in the same direction, or in directions alternately opposed, or again, the separate influence of the direct or the inverted currents. The simple induction of the inductor on itself is obtained with a reel with a single wire in place of the conductor  $\alpha$ , and the arrangement described (122.).

125. It remains for me to give some details on the construction of the rheotrope. The three metallic wheels  $r, s, t$  (fig. 5) present on their periphery twelve hollows filled in with hard wood. These heterogeneous wheels have been worked together by the lathe; they are each  $0^m\cdot80$  in diameter, and  $0^m\cdot06$  in thickness. A metallic tooth of the middle wheel  $s$  exactly corresponds to one isolating part of the extremes  $r$  and  $t$ . They are placed on the same brass axis  $kl$ , which is turned by a winch  $n$  or a tooth-wheel. The spring  $i$  and the wheel  $t$  are in metallic contact with the axis. The wheels  $r$  and  $s$  are, on the contrary, each isolated from it by an ivory ring covered externally with a brass cylinder. These two cylinders bear the wheels, and are constantly pressed by springs  $g, h$ , which embrace them on a semi-circumference. The three springs  $g, h, i$  terminate on the three heads  $g', h', i'$ , by means of which they can communicate together. Lastly, the six springs  $a, b, c, d, e, f$  are made of plates of hammered copper; they are fixed to the base of the instrument by screws,  $r', s', t'$ , the heads of which, similar to  $g'$ , and pierced like them with two holes, can receive the metallic wires intended to establish a connexion between the different wheels. These springs are cleft in order that the groove may facilitate the adjustment of their length. Above they bear a screw (fig. 6) in the part which has to rest on the circumference of the wheels; the opposite notch allows of regulating the elasticity of the spring and the degree of friction. The play of these pieces may thus be regulated with minute precision.

126. If it is not wanted to impart the same direction to the two induced currents, the apparatus may be simplified by giving it only two wheels. One is reserved to render the current of the battery intermittent; the other is joined to the induced wire; and according as there is coincidence or alter-

nation in the closing of the two circuits, only either the direct or the inverted currents are received. This double effect may be obtained by changing the point of contact with one of the springs, or by varying the position of one of the wheels on the axis relatively to the other. Two wheels do not permit of giving the same direction to the direct and the inverted currents; because as it is evident that the induced circuit must communicate with the two wheels when the principal current is closed, a part of this current may proceed from the wire of induction and modify the effect of the direct induced current.

127. Lastly, if it be desired to isolate only the inverted induced currents, the rheotrope may be reduced to a single wheel. It is sufficient for the proposed object to open the induced circuit when the inducting circuit is closed, and *vice versa*. But this arrangement would not be suited to isolate the direct induced currents, because it would be necessary to close simultaneously the two circuits, and the voltaic current would be propagated in the double channel presented to it.

128. It will be found convenient to mark letters on the different pieces  $g'$ ,  $h'$ ,  $i'$ ,  $r'$ ,  $s'$ ,  $t'$ , and to repeat them at the extremities of the metallic conductors employed to connect these pieces. These conductors will be fixed to the interior of the lid of the case which contains the whole electro-electric machine; and a brief direction will indicate which ought to be employed to produce the effects corresponding to the different possible cases.

129. It is understood that the commutator with three or with two wheels is applicable to all magneto-electric machines, telegraphs, clocks, &c., whose motive principle is the electricity of the magnet or of the battery.

#### § XV. Employment of induced currents to restore sensation.

130. The cases of nervous weakness which have yielded to a judicious application of electro-physiological shocks and discharges are too well ascertained to admit of any question. Since the marvellous effects of æther have been known, I have proposed to several physicians the employment of the electro-electric machine, or at least of intermittent currents of very short duration, to obviate the dangers which the injection of too strong a dose of this liquid, or a too prolonged inhalament of it, might produce. I have made some experiments\* with a view to verify the accuracy of my expectations; and although they are so few as to require to be repeated and varied, I shall

\* In company with Dr. A. P. Prevost, and Mr. Schnetzler. I take this opportunity of thanking these gentlemen for their zealous cooperation.

give them here, because similar results have recently been announced by M. Ducros\*.

131. The animals subjected to experiment were a rabbit three months old, a chicken nine months old, and some frogs of both sexes. They are all very sensitive to electric shocks. The action of æther upon them is also very powerful, especially on the frogs, which should not be moistened with this liquid.

132. The rabbit and the chicken appeared to have recovered their sensation sooner under the influence of the shocks of induction than by simple exposure to the air. In the frogs no difference in this respect was remarked.

133. The ætherization was effected by plunging the animal into a glass cylindrical vessel, in which boxes were arranged furnished with sponges moistened with æther; it was covered with a piece of linen dipt in water. The internal atmosphere was removed from time to time by removing the covering.

134. The most remarkable case was presented by the chicken. A quantity of æther, more than sufficient to produce insensibility, was injected into its rectum. When it arrived at this state, two or three shocks of the electro-electric apparatus (110.) were passed from one wing to the opposite leg, which shocks were effected by a Grove's pair; immediately the eyes opened. On continuing the discharges in a very intermittent manner, the animal was seen to struggle, to rise on its feet, and then to fly to the end of the laboratory, relapsing gradually into an insensible sleep under the influence of the portion of injected æther which had not as yet produced its effect.

135. The rabbit and the chicken were subjected to several successive ætherizations. The former, young and weak, died six or seven hours after the fourth trial (injection). At the end of fifteen hours its body was stiff, as if death had resulted from natural causes. Its nerves exhibited the softening mentioned by some anatomists. The chicken, on the contrary, survived, and even on the following day laid an egg with a soft shell. It subsequently produced several others perfectly healthy. It did not appear to feel the effects of the shocks or injections to which it had been subjected. It ate corn greedily, and the rabbit lettuce leaves, as soon as the stupefaction produced by the æther had terminated.

136. Experiments were made on the frogs and the chicken; one while with the effect of the induced currents successively

\* *Comptes Rendus de l'Académie des Sciences de Paris*, sitting of the 22nd of February 1847, p. 286.

direct and inverted, at another with inverted currents only, employing the arrangement above described (127.). There was no perceptible difference between the two methods of electrifying, even on circulating the inverted currents from the feet to the wings, or *vice versa*.

### § XVI. Action of Induced Currents on Albumen.

137. Brande was the first who pointed out the coagulation of albumen on the positive pole of the battery. M. Matteucci, in treating of the physiological action of electric currents \*, says, that if the pole which was first positive be rendered negative, the albumen is not seen to redissolve, and that consequently an electric current may very well produce a cataract, but not destroy it. On the other hand, Prof. Zantedeschi affirms that he has seen the liquefaction of the albumen at the negative pole†. Repeated experiments have never shown me this return to the fluid state, and lead me to adopt entirely the conclusion of the celebrated physiologist of Pisa.

138. The coagulation of albumen does not present any remarkable phase, when, under the immediate influence of a battery, we substitute either direct or inverted induced currents, or the voltaic current rendered intermittent and strengthened by the reaction of the induction which it has engendered in its own conductor and in the neighbouring conductor (124.). But the phænomenon changes when the liquid is traversed by induced currents in alternate directions.

139. Through the inducting wire A of an electro-electric machine furnished with a bundle of iron wires, I passed the current of five Grove's pairs of  $0^{\text{m}}\cdot 1$  square surface. The extremities *x* and *y* of the induced wire B (fig. 7) terminated in cups *gg* full of mercury. The circuit was closed by two platina wires *a*, *b* of  $1^{\text{mm}}$  in diameter, one part immersed in the cups, the other in the glass *o* full of the white of egg. The latter immediately coagulated around each wire, especially round that which communicated with the extremity of the circuit B, from whence proceeded the inverted induced current, and which corresponded to the positive termination of the rheophorus A. At the end of a few minutes some bubbles of gas appeared on the circumference of the coagulum. Some, having increased in volume, rose lightly to the surface of the viscous medium in which they were formed. The albumen, riddled with holes, by which the gas escaped and continued

\* *Lezioni sopra i fenomeni fisico-chimici dei corpi viventi*, p. 173. Pisa, 1844.

† *Trattato del Magnetismo et della Elettricità*, vol. ii. p. 511. Venice, 1845.

to be disengaged, turned black in several places: then a series of *luminous sparkles*, and lastly real sparks of a bright yellow glittered on the whole immersed part of the platina wire. At the same time the induced wire B was heated around the reel, the metallic pieces of the rheotrope rose in temperature, and the upper sides of the glass, not filled with the albumen, were coated with aqueous vapour.

140. This remarkable phænomenon is doubtless complicated. The coruscations do not dart from one wire to the other in the liquid; they are seen along the wire. I thought at first that the combustion (for it was such) only took place on one of the electrodes (139.); but on repeating the experiment many times, I saw it alternate on both of them according as I reversed the poles of the battery, or present itself first upon one wire, then upon the other, without the direction of the current being changed; or lastly appear upon only one of them, whatever changes were made in the positions of the rheophori and the extremities of the induced circuit. I attribute this latter case, which only occurred when the surface of the albumen was covered with a layer of æther, to the difference of the conditions of contact of the two platina electrodes with the liquid: one, in fact, was then only covered with a slight coagulum, whilst the other gave rise to a considerable quantity of gas. These gases were collected on the æther in a tube traversed by a platina wire cemented at its top. They presented neither free carbonic acid, nor oxygen, nor hydrogen. I think that they were a mixture of oxide of carbon and carburetted hydrogens.

141. The albumen solidified around platina conductors acquires the consistence of very soft glue; it is ductile, brownish, even blackish, and diffuses a marked odour of burnt horn or phosphoretted hydrogen. The platina does not take the pulverulent appearance nor black colour which are communicated to it by discontinuous alternate currents in other media; it preserves its metallic appearance. With the assistance of Prof. Marignac I analysed the coagulum; it contained no trace of platina. There is therefore here no catalytic action.

142. These various remarks lead me to think that, in circumstances of imperfect conductivity of the albumen, and of great power in the induced currents employed, the immersed wires become heated when the coating of coagulum and of gaseous bubbles has put a new obstacle to the passage of the alternate currents (an obstacle rendered evident by the elevation of temperature of the external circuits), whence results a true igneous decomposition and a burning, under the influence of oxygen in a nascent state, of combustible elements exposed.

143. Whatever value this opinion may have, it seems to me that the decomposition of albumen by the passage of very intense induced currents is a fact which deserves the serious attention of physicians and physiologists. The presence of this body in the blood, in urine, in the eye, in amniotic liquors, &c., requires caution in the employment of violent alternate currents.

144. The appearances which I have described equally take place in the albumen extracted from new-laid eggs, immersed for some hours in the vapour of æther. They *appear* even to be developed there more easily.

145. It is perhaps well to add, that the production of these bright coruscations indifferently on the two electrodes negatives any explanation founded on a different polarity of the platina wires, and all analogy with the phænomena investigated by MM. Gassiot\*, Hare†, and Neeff‡.

Geneva, June 18, 1846.

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#### XLI. *On eliminating the Signs in Star-Reductions.*

By S. M. DRACH, F.R.A.S.

*To the Editors of the Philosophical Magazine and Journal.*

GENTLEMEN,

THE subject of this paper was broached by the Astronomer Royal in the Monthly Notices of the Royal Astronomical Society for January 1847. I beg to propose the following extension, eliminating even the indices of the logs. employed.

Let  $A = E - P$ ,  $B = F - Q$ ,  $C = G - R$ ,  $D = H - S$ ;  
 $a = e - p$ , &c.  $a' = e' - p'$  for decl., or  $= p' - e'$  for N. P. Dist.,  
 $P$ ,  $p$ ,  $p'$ , &c. are numerical constants afterwards determined.

$$\text{Corr. R.A.} = \sum Aa = \sum Ee - \sum ep - \sum Ep + \sum Pp:$$

$$\text{Corr. N.P.D.} = \sum Aa' = \sum Ee' - \sum e'P - \sum Ep' + \sum Pp'.$$

Let  $P = 28.75$ ,  $Q = 30.5$ ,  $R = 1.35$ ,  $S = 20$  (R.A. given in time).

I. Right ascension,  $p = 2^{\circ}$ ,  $q = 2$ ,  $r = 30.5$ ,  $s = 2$ .

\* *Archives de l'Electricité*, vol. iii. p. 240.

† Silliman's American Journal, January 1841. I succeeded several years ago in melting in an intermittent manner an iron wire of  $2^{\text{mm}}$  diameter, employed as a negative electrode on the surface of impure mercury in which a copper wire bound to the positive pole is immersed. Twenty Daniell's couples, or forty smaller Bunsen's, suffice for this experiment.

‡ *Archives des Sciences Physiques et Naturelles*, vol. i. p. 30.

$$\Sigma Pp - \Sigma eP = -78^s.994 + 41^s.912 \left. \begin{array}{l} \left\{ 1 + \frac{1}{15} \sec \delta \sin \overline{\alpha + 14^h 53^m 14^s} \right\} \\ + 32^s.937 \left\{ 1 + \frac{1}{15} \tan \delta \sin \overline{\alpha + 14^h 18^m 49^s} \right\} \end{array} \right\} . \quad (J.)$$

$$\left. \begin{array}{l} -\Sigma Ep = -308^s.392 + 55^s.422 \{ 1 + \sin \overline{\odot + 42^\circ 32' 4''} \} \\ + 1.324 \{ 1 + \sin 2 \overline{\odot + 55^\circ 29'} \} \\ + 30.5(1-t) + 21.254 \{ 1 + \sin \overline{\alpha + 60^\circ 30' 44''} \} \\ + 0.217 \{ 1 + \sin 2 \overline{\alpha + 235^\circ 52'} \}. \end{array} \right\} \quad (K.)$$

Sum =  $\Sigma Aa - \Sigma Ee = -387^s.386 + \text{periodical terms.}$

II. North Polar Distance,  $p' = 2$ ,  $q' = 2$ ,  $r' = 30.5$  s = 2.

$$\left. \begin{array}{l} \Sigma Pp' - \Sigma e'P = -74''.849 + 12''.476 \cos \delta + 41''.912 \\ \{ 1 + \sin \delta \sin \overline{\alpha + 8^h 53^m 14^s} \\ + 32''.937 \{ 1 + \sin \overline{\alpha + 8^h 18^m 49^s} \} \} . \end{array} \right\} \quad (J').$$

$$-\Sigma Ep' = -\frac{\Sigma Ep}{15} = -308''.392 + \&c. \quad (K').$$

Sum =  $\Sigma Aa - \Sigma Ee = -383''.241 + \text{periodical terms.}$

Now if we add to (J.) and (J') the constant 180, and to (K.) the constant 420 seconds, there will be only *positive* quantities, and we shall have merely to subtract  $10^m$  or  $10'$  from the mean place; the corrections being

$$E = 28.75 - 18.732 \cos \odot \quad e = 2 + \frac{1}{15} \cos \alpha \sec \delta$$

$$e' = 2 - 4.34 \cos \delta + \sin \alpha \sin \delta$$

$$F = 30.5 - 20.420 \sin \odot \quad f = 2 + \frac{1}{15} \sin \alpha \sec \delta$$

$$f' = 2 - \cos \alpha \sin \delta$$

$$10G = 13.5 + 10t - 3.43 \sin \alpha \&c. \quad 0.1g = 3.35706 + 0.1337 \sin \alpha \tan \delta$$

$$0.1g' = 3.05 - 2.0055 \cos \alpha$$

$$H = 20 - 9.250 \cos \alpha \&c. \quad h = 2 + \frac{1}{15} \cos \alpha \tan \delta$$

$$h' = 2 + \sin \alpha$$

It follows that the index of the first set in logarithms is constantly *unity*, and that of the third set constantly *zero*, permitting the omission of the latter. From  $86^\circ 10'$  S. dec. to  $88^\circ 50'$  N. dec.  $e, f, g, h$  will have their values range between 1 and 10, and their indices therefore always *zero*; these may also be omitted. Now of the 8377 British Association Ca-

talogue stars, only sixteen fall out of this category in 1850; viz.

Urs. Min. 2320, 4070, 4150, 4165, 6281, 6320, 6999, 7184, Octans, 71, 2878, 5936, 5959, 6793, 7020, 7713, 8072; a satisfactory result, as these polar segments =  $\frac{1}{447}$  th =  $\frac{1}{8377}$  ths of the spherical surface.

With my constants, seven of those sixteen (2320, 4070, 4150, 5936, 6281, 6320, 7713) have all their R.A. coefficients positive, the others have some negative. Indeed, near the pole the annual change is so great, as to render greater constants to include a dozen of these sixteen needless.

The saving in the above 8362 stars permits an additional column, although five fig. logs. are required, giving a result as far as  $0^{\circ}01$  or  $0''01$ .

App. R.A. = mean R.A. at epoch + yearly precession + proper motion + ephemeral quantity.

+ Ee + Ff + Gg + Hh + stellar quantity -  $10^m$ .

App. N.P.D. = similar quantity -  $10'$ ,

which  $10'$  might be already included in the mean place, as in the planetary tables. The ephemeral quantity (depending on the day of the year) is the same in R.A. *time-seconds*, or N.P.D. *space-seconds*.

Possibly these hints may be useful before reprinting the British Association Catalogue.

S. M. DRACH.

London, Sept. 2, 1847.

## XLII. On the Molybdate of Lead. By Mr. JOHN BROWN\*.

MOLYBDATE of lead was first analysed by Klaproth†, who proceeded in the following manner:—

100 grains of the mineral finely pounded were treated with dilute hydrochloric acid, and the whole of the silica was thus separated. Upon cooling, the greater part of the chloride of lead was deposited in fine crystals. The clear supernatant liquor was then drawn off, and when sufficiently concentrated the remaining chloride of lead was deposited. The whole of the chloride was then carefully collected together, dried and weighed. Its weight was 74·5 grs. From this the quantity of oxide of lead was ascertained, which was 64·42 grs. Every 100 grains of molybdate of lead contain therefore 64·42 grs. of oxide of lead. When the solution had thus been freed from lead, it was concentrated by evaporation. Nitric acid was

\* Read before the Philosophical Society of Glasgow, April 28, 1847, and communicated by Dr. R. D. Thomson.

† *Beiträge zur chemischen Kenntniss der Mineralkörper*, vol. i. 265.

then added to the solution, which immediately became of a fine blue colour. When sufficiently concentrated, a quantity of molybdic acid separated. The solution was then evaporated to dryness, and the molybdic acid remained in the form of a fine citron-yellow powder, which when completely dried weighed 34.25 grs.

The constituents therefore of 100 parts of the purest crystals of Carinthian molybdate of lead are—

Oxide of lead . .	64.42	59.59}	corrected from the
Molybdic acid . .	34.25	34.25}	chloride.

As Klaproth did not know the true composition of chloride of lead, the quantity of PbO given above is wrong. Calculating the quantity of oxide from the quantity of chloride which he obtained, we get 59.59 per cent. of oxide of lead, which is very near the theoretical quantity, or 60.57. But the great error is in the molybdic acid. What Klaproth considered as silica, was very probably molybdic acid, as that acid is not entirely soluble in hydrochloric acid; and as he apparently deducted this as impurity, he gets too little molybdic acid. He also does not mention how he washed out the molybdic acid from the chloride of lead. It could not well have been done with water, for chloride of lead is soluble to a great extent. This is a great point of imperfection in the analysis.

II. This mineral was next subjected to a close examination by Charles Hatchett, Esq., whose analysis is recorded in the Philosophical Transactions (vol. xviii.), of which the following is a summary :—

250 grs. of the ore, freed from as much impurity as possible, were put into a glass flask, and digested with sulphuric acid for some time under a strong heat. When the solution cooled, the clear liquor was drawn off, and the residual sulphate of lead washed by subsidence. This process was repeated several times. The acid solutions were then filtered, and the filtered liquid neutralized by caustic ammonia. After standing for twenty-four hours a pale yellowish-coloured precipitate fell down, which was collected on a filter, washed and dried: its weight was then 4.20 grs. It had a yellowish colour, and when dissolved in hydrochloric acid gave a blue precipitate with yellow prussiate of potash.

Part of the clear blue solution, which was composed of sulphate and molybdate of ammonia, was then put into a retort and evaporated down, the rest of the solution being added as the liquid in the retort evaporated; the whole was then dried and strongly heated. In this manner all the sulphate of ammonia was driven off, whilst the molybdate of ammonia was decomposed into molybdic acid and ammonia, the former

of which remained in the retort: the molybdic acid then weighed 95 grs. The sulphate of lead formerly obtained was then treated in the following manner:—It was boiled with four ounces of carbonate of soda in solution; the powder was then washed, and nitric acid much diluted was poured on it. The whole dissolved except a small quantity of silica, which was thrown on a filter: this when washed and dried weighed .7 gr. The acid was then exactly neutralized with caustic potash, which precipitated the lead as oxide: this, when washed and dried, weighed 146·00 grs.

The oxide of lead was then dissolved in nitric acid, and sulphuric acid was added. After standing for some time the solution was filtered and the filtered liquor saturated with  $\text{NH}_3$ : after standing for some time a small quantity of peroxide of iron was precipitated, which when filtered and dried weighed 1·0 gr. This, when added to the former quantity of peroxide of iron, makes the quantity 5·2 grs., and the quantity of oxide of lead 145 grs.

The composition of 250 grs. of molybdate of lead is therefore—

	per cent.
Oxide of lead . . . . .	58·00
Molybdic acid . . . . .	38·00
Peroxide of iron . . . . .	2·08
Silica . . . . .	·28
	<hr/>
245·9	98·36

If the iron and silica be subtracted as impurities, this analysis is very correct; but the method is very tedious and inconvenient, and requires very great care.

III. The next person who turned his attention to this mineral was Göbel\*.

100 grs. of the mineral were digested with dilute hydrochloric acid with the assistance of heat: upon cooling, the lead was deposited in the form of chloride. These crystals were then collected together and dried; the weight was then found to be 72·5 grs., which is equivalent to 59 grs. of oxide of lead. The solution freed from lead was evaporated to dryness: when perfectly dry a small quantity of nitric acid was added, and the solution was again dried. It was then heated to redness in a close vessel and weighed: its weight was thus found to be 40·5 grs.

100 grains contain therefore—

\* Schweigger's *Journal für Chemie und Physik*, vol. xxxvii. 71.

Oxide of lead . . .	59·0	58·0	corrected from the chloride.
Molybdic acid : : .	40·5	40·5	
	99·5	98·5	

This method is essentially the same as that used by Klaproth. The result however is much nearer the truth. Göbel however gets too much molybdic acid and too little oxide of lead. This was probably owing to some of the chloride of lead not being obtained, as it is soluble to a great extent in water (1 in 152 of water)\*; and the analyst does not state how he washed the chloride of lead free from molybdic acid.

IV. The methods hitherto employed being liable to very great objections, the molybdate of lead was analysed by another method, which had proved successful in the hands of Mr. William Parry last year in the Glasgow College laboratory.

26·84 grs. of the mineral finely pounded were boiled for a considerable time with nitric acid and filtered. The undecomposed mineral, along with a quantity of molybdic acid, remained on the filter. This was then completely washed: ammonia was then poured into the filter. The molybdic acid was thus dissolved, and the insoluble matter remained on the filter; this was then washed, dried, ignited and weighed. The weight of the insoluble matter in 26·84 grs. was 1·15 gr.

The solution containing the molybdate of ammonia was then evaporated to dryness, and heated to redness in a close vessel. The greater part of the molybdic acid was thus obtained. Its weight was 6·76 grs.

The first washings from the molybdic acid and the insoluble matter were then concentrated. Caustic ammonia was added in order to neutralize the excess of acid, and afterwards sulphohydret of ammonia was added in excess. In this manner the lead was precipitated in the form of sulphuret, while the tersulphuret of molybdenum was redissolved in excess, giving the solution a deep red colour. The sulphuret of lead was then thrown on a filter, and washed with water containing sulphohydret of ammonia. When completely washed, the sulphuret of lead was dissolved in muriatic acid, and after boiling for some time was filtered to get rid of the sulphur. The filtered liquor was then concentrated, and the lead precipitated by means of oxalate of ammonia. The precipitated oxalate of lead was then thrown on a filter, washed and dried. By ignition the oxalate of lead was converted into the oxide;

\* I found in two experiments that 3963 grs. of water at 60° dissolved 26·2 grs. Pb Cl = 1 in 151, and 4260 grs. HO dissolved 27·6 grs. Pb Cl = 1 in 154 HO.

the quantity of which in 26·84 grs. was thus found to be 16·20 grs., which is equivalent to 60·35 per cent. of oxide of lead.

The next thing to be obtained was the rest of the molybdic acid. This was contained in the washings from the sulphuret of lead in the form of tersulphuret of molybdenum. When the solution was sufficiently concentrated, it was made slightly acid by means of nitric acid: a brownish-coloured precipitate fell down, which is tersulphuret of molybdenum. This was then thrown on a filter and washed. It was then dried at 212° and weighed: its weight was 3·37 grs. From this and the previous quantity of molybdic acid the quantity per cent. was calculated, which was 39·30 grs.

According to this analysis, the composition of molybdate of lead is—

Molybdic acid . . .	39·30
Protoxide of lead .	60·35
	99·65

V. In the course of the preceding analysis it was observed that the sulphohydret of ammonia exercised a powerful solvent action on the mineral itself. The following new method of successfully analysing this mineral was therefore adopted.

23·0 grs., after being reduced to a very fine powder, were digested with the aid of heat in sulphohydret of ammonia. The solution became immediately of a deep red colour, owing to the tersulphuret of molybdenum which was held in solution by the sulphohydret of ammonia, while the lead was precipitated as sulphuret, and fell to the bottom in the form of a black powder. The clear supernatant liquor was then drawn off, and a fresh portion of sulphohydret of ammonia was added. This, after standing for some time, was thrown on a filter, and washed with water containing sulphohydret of ammonia. The tersulphuret of molybdenum passed through in solution, while the sulphuret of lead remained on the filter. When this was completely washed it was dissolved in dilute muriatic acid, which took up the sulphuret of lead and left the undecomposed matter along with the sulphur. These were then thrown on a filter and washed: the whole was then burnt. The sulphur was thus driven off, while the insoluble matter remained. The insoluble matter in 23 grs. amounted to 24 gr., whilst in the former analysis it amounted to 1·15 in 23 grs.

When the washings from the sulphur were sufficiently concentrated, the lead was precipitated by means of ammonia and oxalate of ammonia. The oxalate of lead was then thrown on a filter and weighed. The quantity of oxide of lead in

22·76 grs. amounted to 13·71 grs., which is equivalent to 60·35 grs. per cent.

The next point was to precipitate the tersulphuret of molybdenum. This was done by making the solution in sulphohydret of ammonia slightly acid by means of muriatic acid. The tersulphuret went down in the form of a brownish-coloured precipitate. This was then thrown on a filter, dried, ignited and weighed. The quantity in 22·76 grs. was thus found to be 9·91 grs., which is equivalent to 39·13 per cent. of molybdic acid.

The constituents therefore of molybdate of lead according to this analysis are—

Molybdic acid . . .	39·19
Lead protoxide . . .	60·23
	99·42

Phosphates and arseniates of lead were decomposed in the same manner; and it is evident this process would also answer with antimoniates, vanadiates and seleniets.

	Klaproth.	Hatchett.	Göbel.	Parry.		J. Brown.			Theory.
Molybdic acid ...	34·25	38·00	40·50	*40·40	39·88	39·30	*40·64	39·19	39·13
Protoxide of lead	59·59	58·00	58·00	59·60	59·56	60·35	59·36	60·23	60·87
Peroxide of iron	.....	2·08							
Silica .....	.....	·28							
	93·84	98·36	98·50	100·00	99·44	99·65	100·00	99·42	100·00

#### Note by Dr. R. D. THOMSON.

*Test for Arseniates, &c.*—I may notice a simple and quick method of testing minerals containing arsenic in its various forms, phosphates, molybdates, vanadiates, &c. A few grains of the mineral to be examined are to be finely pulverized in an agate mortar and introduced into a test-tube, and boiled with bisulphohydret of ammonia for a few minutes. The mineral is partially decomposed; the sulphuret of lead precipitates, while sulphuret of arsenic, &c. is dissolved by the excess of the reagent. The tube is then allowed to stand at rest, and the supernatant liquor poured off or filtered. The excess of bisulphohydret of ammonia being removed by evaporation, the yellow sulphuret of arsenic precipitates. A molybdate is

\* In these analyses the lead only was ascertained, and the deficiency was taken as molybdic acid.

The two last analyses were made by means of sulphohydret of ammonia, the three preceding by nitric acid.

detected at once by the fine orange-red colour which the reagent assumes when it is heated in contact with that mineral.

A vanadate gives a dark colour, but possessing less of the red shade than the molybdate. The liquor filtered from the sulphuret of lead containing the vanadium in solution has a green colour, becoming blue by the addition of hydrochloric acid. Hence it appears that arsenic dissolved in bisulphohydret of ammonia does not alter the colour of that reagent, while the liquor gives a precipitate of orpiment by concentration. Molybdenum and vanadium, on the other hand, render that reagent reddish, and give brown precipitates by concentration. The liquor filtered from the sulphuret of molybdenum is colourless, or its hue is similar to that of the reagent, while the liquor derived from the vanadium precipitate is *green*.

I have succeeded in decomposing a sufficient amount of these minerals for quantitative analysis by the preceding process when they have been carefully pounded and levigated. The process is particularly advantageous in the analysis of molybdate of lead, where the use of nitric acid for dissolving the mineral is objectionable in consequence of its tendency to form the molybdate of molybdenum, and where hydrochloric acid, by producing a chloride of lead, renders the employment of an inconvenient quantity of water necessary. I have found this process for testing very convenient where it was desirable to use minute quantities of crystals, and where rapidity is an object in view, as in examining a large collection of minerals of the preceding description; and I mention it for the sake of those who may possess in their cabinets minerals of this nature which they may desire to test, since it may be found a useful adjunct to the blowpipe test.

The bisulphohydret affords a simple distinguishing test between metallic arsenic and antimony, when spots have been received on porcelain by Marsh's process. Arsenic dissolves in the reagent, and leaves a yellow stain by evaporation. Antimony dissolves and leaves an orange stain. For this experiment it is convenient to use the inside of the cover of a porcelain crucible.

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*XLIII. On Fossil Calamites found standing in an erect position in the Carboniferous Strata near Wigan, Lancashire. By E. W. BINNEY\*.*

THE fragmentary condition of the great bulk of fossil plants found imbedded in the coal measures has led many geologists to suppose that they had been drifted from adjoin-

\* Read before the Literary and Philosophical Society of Manchester, July 6, 1847, and communicated by the Author.

ing lands, and had not grown in the position in which they are now found. But although it is certain that plants which have been drifted by water generally present a broken appearance, it is equally true that plants grown upon the spots where they are now found, having been laid low by the action of currents of water, or weighed down and buried by the weight of mud or silt that had fallen upon them, afford similar appearances, so that great care must be taken before we conclude that a plant has not grown on the place where it is now found merely because we find it in fragments.

A few years ago the whole of the fossil flora was generally supposed to have been drifted. The first plant that was excepted from this rule and recovered its proper place was the *Stigmaria*, whose long stringy rootlets prevented it from being so conveniently drifted by currents as the advocates of the *drift* hypothesis could desire; therefore it was allowed to have grown where it is found.

When numbers of *Sigillariae* were found standing erect on seams of coal, and their roots had not been traced to their extremities, it was at first attempted to refer them to accident, like the snags now found in the Mississippi and other rivers. However, a more careful observation of these fossils, and the great number in which they were found, at length induced geologists to admit that they must have grown where they are now met with. The discovery of the trees at Dixon Fold on the Manchester and Bolton Railway by Mr. John Hawkhaw, F.G.S., and so ably described by the late Mr. Bowman, F.G.S., in the first volume of the Transactions of the Manchester Geological Society, mainly contributed to establish this view, which has been since clearly proved by the certainty that *Stigmariae* are the roots of *Sigillariae*, as the fossil trees of St. Helens and Dukinfield testify.

As yet, however, *Sigillaria* was the only tree that to any extent could be said to have been discovered *in situ*.

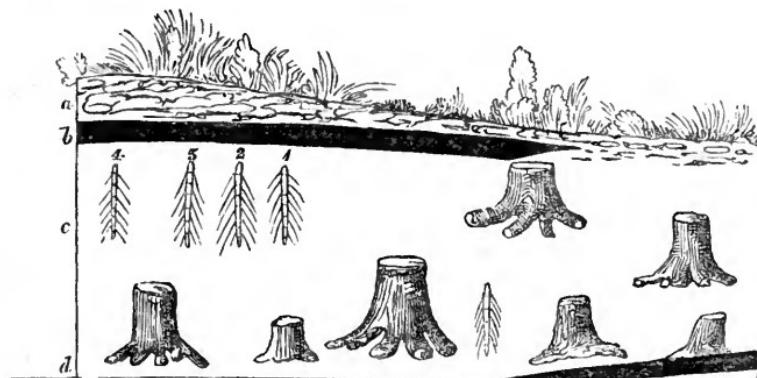
In the present communication, it is intended to show that *Calamites* have been found standing erect on the places in which they grew by the side of *Sigillariae*, and that the rootlets of the former very much resemble, if they are not identical with, those of the latter plant.

The rootlets of *Calamites* have been very correctly figured and described by Messrs. Lindley and Hutton in vol. i. pp. 78 and 79 of their *Fossil Flora of Great Britain*; but it is believed by the writer that although numbers of erect *Calamites* have been observed in the coal-measures, still none of them to his knowledge have been described with their roots standing in the position in which they had grown.

During an examination of the deep excavations through the coal-measures made in forming the Bury and Liverpool Railway in the vicinity of Wigan, I was so fortunate as to discover on the 21st day of April last, in the Pemberton Hill cutting about two miles west of Wigan, not only a whole forest of *Sigillariæ* standing erect with their roots just as they had grown, but also many *Calamites* in a similar state of perfection.

The accompanying woodcut, fig. 1, representing a view of the south side of the railway cutting, will show the position in which the fossils occurred, although it is on an exaggerated scale, and the characters of the trees are not given.

Fig. 1.



The excavation in which the fossils were met with is about twenty-five feet deep, and consists chiefly of a light gray-coloured silty clay known by the provincial name of "Warren," containing nodules of ironstone. This deposit is very similar in composition to the strata in which the fossil trees at St. Helens and Dukinfield before described were found. It lies between two beds of coal each about two feet in thickness, and occupies a position in the higher part of the middle division of the Lancashire coal-field. The upper seam of coal is covered, and in some places partly removed, by a deposit of one or two yards in thickness of till. Near the bridge is seen a flexure in the strata, as shown in the woodcut.

In Mr. Haliburton's section at Haigh (vol. vi. New Series, of Manchester Memoirs, p. 437, Remarks on the Coal District of South Lancashire, by James Heywood, Esq., F.R.S.), occur the following strata:—

	yards.	ft.	in.
Depth from the surface . . . . .	10	0	0
Coal which burns to a white ash . .	1	0	6
Interval . . . . .	8	0	0
Coal (Wigan yard coal) . . . . .	0	2	6
Interval . . . . .	16	0	0
Coal . . . . .	0	2	6
Interval . . . . .	24	0	0
Coal (Wigan four-feet coal) . . . . .	1	1	0
Interval . . . . .	32	0	0
Coal (Wigan seven-feet coal) . . . . .	2	1	0

The interval of eight yards is in my opinion the deposit in which the fossil trees were met with.

In a distance of about fifty yards of the cutting, on my first visit to the place, I observed full thirty upright stems of *Sigillariæ*, besides several flattened ones lying in a horizontal position. These trees exhibited no evidence of their former structure, being mere casts, having their insides filled with a similar material to the matrix in which they were found imbedded. Their outsides consisted of a coating of bright coal of about a quarter of an inch in thickness, and were ribbed and formed as *Sigillariæ* usually are. In diameter they varied from one to three feet: their heights ranged from two to twelve feet; but, with one exception of a stem with another lying directly across it, none of them could be traced to their termination upwards. Some of them rested with their stems on the top of the lower seam of coal; others had their roots midway between the two seams; and others again were found just under and in the floor of the upper seam. Most of the trees, which on exposure retained their coaly envelope, presented the irregularly ribbed and furrowed appearance which the Dixon Fold and St. Helen's trees exhibited, and which some geologists contend are not sufficient to identify them with *Sigillariæ*; but six specimens were decorticated, and showed well-defined scars and all the other characters of *Sigillaria reniformis*, *alternans* and *organum*. All the upright trees had roots of *Stigmariæ* with their rootlets traversing the silty clay in all directions.

Many stems of *Calamites* were found standing erect amongst the last-described trees, some of which were traced four and five feet in height without reaching their tops. These stems varied in diameter from one to five inches: they showed no structure internally, being mere casts filled with silty clay and having a coaly envelope of about one-sixth of an inch in thickness, which on being removed exposed the ribbed character

and usual joints of this genus of plants. All those which could be traced downwards exhibited rootlets proceeding from the lower joints, less in size, but resembling those of *Stigmariæ*.

One of the erect *Calamites* was traced for about two feet upwards, and then at first sight appeared to terminate; but on more careful inspection it could be traced running in a horizontal direction, but so much compressed as to remain unseen without very close observation.

The erect stems both of undoubted *Sigillariæ* and trees which did not exhibit all the characters of *Sigillariæ* as well as those of *Calamites*, occurred in all parts of the deposit of silty clay, from the top of the lower seam to the floor of the upper one.

In the deposit where the trees occurred were found plants of the genera *Neuropteris*, *Pecopteris*, *Sphenopteris*, *Cyclopterus*, *Odontopteris*, *Asterophyllites*, *Pinnularia*, *Lepidodendron*, *Lepidophyllum*, *Lepidostrobus*, *Lycopoides*, *Sphenophyllum*, &c.

Having thus given a hasty sketch of the locality where the fossils occurred, and the fossils themselves as they appeared to me on my first visit to the place, I shall proceed to describe some erect stems of *Calamites*, which are intended to form the chief subject of this communication. These trees were not only seen by myself, but by Dr. J. Hooker and M. Jobert, two well-known geologists; and it is to the latter gentleman that I am indebted for the drawings which accompany this paper.

On the 22nd of May last, in company with the above-named gentlemen, I again visited the Pemberton Hill cutting. Many erect specimens of *Calamites*, both with and without roots, had been seen on my previous visits to the place; but the three which it is now my intention to describe exhibited the lower terminations, and more distinctly showed the rootlets than the other specimens.

The three fossils marked Nos. 1, 2 and 3, in the rough sketch before given, and No. 4, an individual examined by me on a previous visit, occurred in the excavation on the south side of the railway. They were all found standing in an erect position about two yards distant from each other, having their tops, as far as bared, two yards under the upper seam of coal. They were each exposed from twenty inches to two feet, and all presented the same external characters with regard to their stems, joints, and rootlets, and most resembled the *Calamites approximatus*.

The description of No. 1 will serve for the other two.

This specimen appeared standing in the silty clay in a nearly

erect position, with the exception of a slight bend in its upper part, as shown in the drawing. It was almost cylindrical, and measured twenty-one inches from the base to its highest part, which was exposed. Its greatest diameter, which occurred near the top, was one and a half inches; it then tapered slightly towards the bottom, and terminated in a club-shaped end. The exterior was covered with a coating of fine coal of about one-eighth of an inch in thickness, which on being removed exposed the usual ribs, furrows and joints, characteristic of *Calamites*. The interior showed no trace of structure, being composed of the same kind of silty clay as the matrix in which the fossil was found.

The following is a sketch of No. 1 as it appeared in the cutting, one-eighth the natural size of the fossil. The upper part had been removed before we saw the specimen.

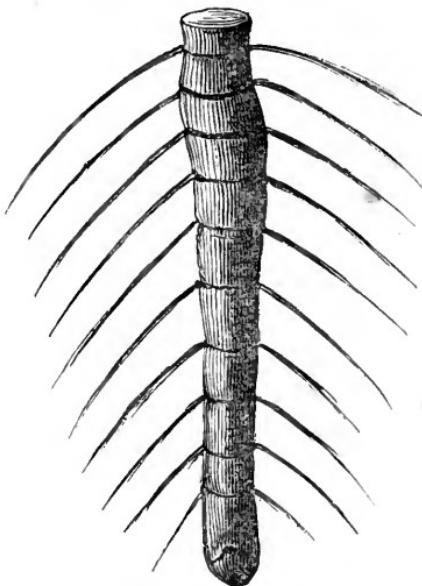
The joints or nodi were ten in number, and occurred at irregular distances, but nearer together at the upper and lower extremities than in the middle of the fossil.

At the joints small circular depressions were seen, from which proceeded rootlets. These could be traced from eight to eleven inches in length without reaching their terminations. They went down into the silty clay, the higher ones making an angle of about  $15^{\circ}$  with the horizon; but the angle gradually increased as they went lower, until they at last described an angle of about  $45^{\circ}$ .

The rootlets appeared to have been originally cylindrical and about one-eighth of an inch in diameter; but they were now compressed, and their outsides covered with a thin coating of carbonaceous matter. On a careful removal of the outside a delicate longitudinal stria could be perceived on the rootlets; there also appeared something like a pith in their middle.

Altogether the rootlets could not be well distinguished from those of *Stigmaria*. They also appeared to come from the

Fig. 2.



stems in something like quincuncial order, like the rootlets of the last-named plant; but of this circumstance I cannot speak with absolute certainty.

The specimen No. 4 differed from the other three only in its base, which did not terminate in the same club-shaped extremity which they did; but after the joints had gradually approximated it turned inwards, and it could not then be seen whether it ended or was inserted into some other stem.

In addition to the above there were many *Calamites*, both in erect, inclined, and horizontal positions, but no leaves or branches were satisfactorily traced to them.

In the course of his examination of upright stems of *Sigillariæ* in the coal-measures, the writer has nearly always found *Calamites* associated with them. At St. Helens they were abundant, and their bases were found in contact with the main roots of *Sigillariæ*. One of the authors of the Fossil Flora, Mr. Hutton, in describing the Burdiehouse fossils at page 24, vol. iii. of that work, states as follows: "Amongst vegetables, the characteristic fossils of this deposit are *Lepidostrobi*, *Lepidophyllites*, *Lepidodendra*, and *Filicites*; the rarity of *Calamites*, which occur but seldom, and of a diminutive size, and the almost entire absence of *Stigmaria*, are very striking to those who are accustomed to view the fossil groups usually presented by the beds of the carboniferous formation; whilst the profusion of *Lepidostrobi* and *Lepidophyllites* of various sizes and in various stages of growth associated with the stems of *Lepidodendra* and those of no other plant, is an additional argument for the opinion which has always appeared highly probable, that they were the fruit, leaves and stem of the same tribe of plants. Of *Sigillaria*, a plant which in the flora of the carboniferous group generally is of so much importance, we could not observe a trace."

In the course of his own observations, the writer has never yet been able to meet with a stem of *Sigillaria* of so small a size as six inches in diameter, or a *Calamites* of so large a size as that. Doubtless there must have been young *Sigillariæ* whether or not there were large *Calamites*. Now what are young *Sigillariæ*? This is a question which yet remains to be answered.

It is now admitted that little is known about the true nature of the genera *Sigillaria* and *Calamites*, except that they were not the hollow succulent stems which they were once supposed to be.

The rootlets of *Calamites*, as previously shown, if not actually identical with, at least very much resemble those of *Sigillaria*. In some specimens of this latter genus, especially those

of the species *approximatus*, figured and described in plate 216, vol. iii. of the Fossil Flora, and the *cruciatus*, figured in plate 19 of Brongniart's *Histoire des Végétaux Fossiles*, their rootlets are arranged in regular quincuncial order. In the largest Calamites that to my knowledge has been figured, namely, that called *Gigas*, plate 27 in Brongniart's work before alluded to, the ribs and furrows begin to appear very like those of *Sigillaria*, and the joints show indistinctly. The termination of the root of a Calamites is exactly of the same form as the terminal point of a *Stigmaria*, both being club-shaped.

I am not aware that up to the present time much, if anything, is known of the structure of Calamites; but if it should resemble that of *Sigillaria*, it may tend to prove that Calamites are but young *Sigillaria*.

In our observations it must not however be lost sight of, that no central axis or pith has to my knowledge yet been discovered in the stem of the Calamites like that found in *Sigillaria*. Both plants are proved to have had similar *habitats*, and therefore it is very probable that they might have had rootlets resembling each other without being the same plant. Still, however, as *Sigillaria* was so long considered a separate plant from *Stigmaria*, it is unphilosophical to take no notice of the analogies of what are now considered distinct genera. Although it will not by any means be safe to affirm that *Sigillaria* and Calamites are the same plant from their analogies, still it is conceived that sufficient evidence has been adduced in this paper to prove that the latter as well as the former plants have generally grown on the places where they are now found, and that the reason why one is so much more frequently found in an erect position than the other, arises from the circumstance of the stem of the one being much stronger than that of the other. A deposit of mud on the branches and leaves of the slender stem of a Calamites might weigh it down and prostrate it, whilst the stout trunk of the *Sigillaria* would resist such action and continue erect.

**XLIV. Upon the Chemical Constitution of Metacetonic Acid, and some other Bodies related to it. By E. FRANKLAND, Esq. and H. KOLBE, Ph.D.\***

THE researches into the constitution of organic compounds certainly belong to the most interesting in chemistry. But they are always attended with more or less danger, and those who, leaving the safer road of experiment, plunge into the depths of hypothesis, and build up theories apparently

\* Communicated by the Chemical Society; having been read April 19, 1847.

ingenious, though often untenable, frequently stumble and fall amongst a host of contradictions. It is a common error, as experience teaches, into which young chemists are very apt to fall, that, persuaded of the infallibility of their own views, and blind to well-founded objections, they endeavour to convince by quick and ready argument rather than by solid reasoning, and consequently they either offend others or feel themselves offended when contradicted.

When in the face of this danger we endeavour to advance views concerning the rational composition of some organic acids which do not accord with those generally received, we do it with a certain degree of timidity, and with the most strenuous endeavour to avoid those causes of error which have been pointed out. It is far from our intention to give a decided preference to the mode of viewing the subject here proposed, or indeed in any way to force our own opinion, nor is it unknown to us that even these views leave many facts unexplained; but we feel convinced that no detriment can accrue to the progress of science by looking at subjects of such importance with an impartial eye from all possible sides.

The starting-point of our experiments was the idea recently expressed by Berzelius, that acetic acid might be considered as a conjugate oxalic acid, as methyl-oxalic acid,  $C_2H_3C_2O_3$ . If this view of the subject, which explains so readily the conversion of acetic acid into chloracetic acid, and the remarkable reconversion of the latter into the former, and which has been further confirmed by the analogous relations of chloro-carbohyposulphuric acid and methyl-hyposulphuric acid, is correct, then the question arises whether it might not be extended to those other acids, so nearly related to acetic acid, namely, formic acid, metacetonic acid, butyric acid, benzoic acid, &c. We are of opinion that this question cannot *à priori* be answered in the negative; on the contrary, it appeared to us, after pursuing the subject further from that point of view, that the manifold metamorphoses which the above combinations undergo might be explained in a very simple manner, and we consequently have submitted the question to careful experimental examination; and we believe that we have gained a fact in support of the theory of conjugate compounds in its application to the acids in question, by the action which cyanide of ethyle exhibits with alkalies and acids.

When benzoic acid is supposed to consist of oxalic acid with the carburetted hydrogen,  $C_{12}H_5$  (phenyle), as a conjunct, then it is evident that benzoë-nitrile obtained by Fehling\* in distilling benzoate of ammonia, must be a cyanogen

\* Liebig's *Annalen*, xlix. p. 91.

compound of the same carbo-hydrogen =  $C_{12}H_5Cy$ . This mode of decomposition of phenyle-oxalic acid becomes thus completely analogous to the well-known formation of cyanogen by heating oxalate of ammonia, and to the formation of hydrocyanic acid from the formiate of ammonia.

Benzoe-nitrile, viewed as cyanide of phenyle, would then, together with the analogous body recently discovered by Schlieper\*, valero-nitrile ( $C_8H_9Cy$ , cyanide of valyle), become allied to cyanide of ethyle; and as these bodies in contact with alkalies are so easily transformed into benzoic acid and valerianic acid, it is to be presumed that cyanide of ethyle under similar circumstances would become transformed into ammonia and metacetonic acid.

We prepared for this purpose pure cyanide of ethyle, according to the process of Pelouze, by the distillation of sulphovinate of potash with cyanide of potassium. The yellow-coloured liquid which passes over† was mixed with water, and separated again by chloride of sodium, dried over chloride of calcium, and lastly distilled in a bent tube freed from air and hermetically sealed. Purified in this manner cyanide of ethyle is a limpid colourless liquid, having an odour much resembling that of the terrible cacodyle. The analysis of the substance gave the following numbers:—

0·219 grm. gave 0·523 grm. of carbonic acid and 0·186 grm. of water.

Theory.

Carbon . .	65·19	6	65·45
Hydrogen . .	9·46	5	9·09
Nitrogen . .	25·35	1	25·46

To settle the question started above, this cyanide of ethyle was added drop by drop to a tolerably concentrated boiling solution of caustic potash, and the product of distillation returned to the retort as long as it retained any smell. During this operation a considerable portion of ammonia was given off. The alkaline residue distilled with sulphuric acid produced an acid liquid, which, neutralized with carbonate of silver, baryta, or lead, gave the corresponding salts of those bases. We had previously satisfied ourselves, by a carefully conducted experiment, that no formic acid was present in the acid solution.

The silver salt crystallizes from its aqueous solution in small acicular prisms. It is sparingly soluble in water, and

\* *Annalen der Chemie*, lix. p. 15.

† We found, in contradiction to Pelouze's statement, that cyanide of ethyle is tolerably soluble in water; but when the solution is saturated with common salt, it again separates unchanged and comes to the surface.

the solution becomes blackened on boiling. The crystals dried over sulphuric acid *in vacuo* had the composition of metacetonate of silver.

I. 0·211 grm. gave, when burnt with oxide of copper, 0·153 grm. carbonic acid and 0·055 grm. water.

II. 0·167 grm. gave on careful ignition 0·100 grm. of metallic silver.

Carbon . . .	19·77	6	19·90
Hydrogen . . .	2·89	5	2·76
Oxygen . . .	13·06	3	13·27
Oxide of silver .	64·28	1	64·07
	100·00	15	100·00

The salt of barytes is very soluble in water; the solution of the salt evaporated to dryness and dried for a long time at 212°, gave the following numbers:—

I. 0·339 grm. gave 0·311 grm. carbonic acid and 0·116 grm. water.

II. 0·258 grm. gave 0·211 grm. sulphate of baryta.

		Theory.
Carbon . . .	24·98	25·46
Hydrogen . . .	3·79	3·53
Oxygen . . .	17·58	16·99
Barytes . . .	53·65	54·02
	100·00	100·00

The lead compound has the sweet taste of acetate of lead: it does not appear to crystallize, but dries up to a tough amorphous saline mass. A portion dried at 212° and *in vacuo* gave exactly the quantity of oxide of lead, corresponding to the formula PbO, C<sub>6</sub>H<sub>5</sub>O<sub>3</sub>, namely,—

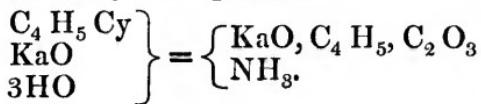
0·446 grm. gave 0·282 grm. oxide of lead and 0·021 grm. metallic lead, equivalent to 63·40 per cent. instead of 63·19.

From the above analyses, there can be no doubt that the acid product of the action of caustic potash upon cyanide of ethyle is metacetonic acid. The same result is produced by weak sulphuric acid (1 part acid to 2 parts water). The silver salt prepared from the acid product of distillation in this case exhibited the properties described above, and an estimation of the oxide of silver gave the following result:—

I. 0·150 grm. when ignited gave 0·090 grm. metallic silver, corresponding to 64·30 per cent. oxide of silver; the theoretical proportion being 64·07 per cent.

The mode of decomposition of cyanide of ethyle described is therefore quite analogous to that of benzoe-nitrile and valero-nitrile; and if metacetonic acid is considered as ethyl-

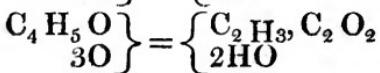
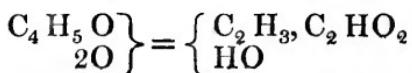
oxalic acid, with the formula  $C_4 H_5 C_2 O_3$ , the decomposition may be expressed by the equation



The assumption will be rendered still more palpable, if, as there is little doubt, at a future period we are able again to produce cyanide of ethyle from metacetone of ammonia.

If, on the contrary, metacetonic acid is considered as an oxide of the radical  $C_6 H_5$ , then it must be assumed, that during the process of oxidation the two atoms of carbon, in the cyanogen, amalgamate themselves, as it were, with ethyle, in order to form the new radical metacetylene. Setting aside the great improbability attached to such an assumption, to which there would be at present no analogous case, we feel justified in giving preference to the former explanation, because it is the more simple, and because it completely agrees with the known transformation of cyanogen and water into oxalic acid and ammonia ; and if, as one of us has found, valerianic acid, placed in the circuit of the voltaic current, by the assumption of 1 atom of oxygen, becomes converted into carbonic acid and the carbo-hydrogen  $C_8 H_9$ , we consider that our view has gained by that fact an additional support, and that the acid in question contains that carbo-hydrogen in conjugate combination with oxalic acid.

The foregoing observations lead to a great simplification of our hypothesis in regard to organic radicals, inasmuch as they do away with the necessity of supposing a specific radical for each acid belonging to an alcohol. The series of radicals which are produced by the addition of one or more equivalents of the carbo-hydrogen  $C_2 H_2$  to 1 equivalent of hydrogen, namely  $C_2 H_3$ ,  $C_4 H_5$ , &c., the hydrated oxides of which form the alcohols, are again found in accordance with our view in the acids derived from them, conjoined with oxalic acid. It may be conceived that the oxygen, in converting alcohol or oxide of ethyle into acetic acid, first acts upon the equivalent of carbo-hydrogen  $C_2 H_2$ , which alone distinguishes ethyle from methyle, and that the successive products of oxidation of this body take up the remaining radical methyle into conjugate combination ; thus in the formation of aldehyde and acetic acid,



Moreover, it cannot be denied that our ideas concerning the functions performed by compound radicals are very much enlarged by these considerations. For when we find methyle and ethyle combining like the electro-positive inorganic elements with the electro-negative non-metallic substances, the property which they also exhibit of uniting with oxalic acid, hyposulphuric acid, and with other, perhaps even neutral, bodies to form conjugate compounds, evinces such an extensive range of properties as is nowhere to be met with amongst the more narrowly defined powers of combination of inorganic substances ; and it is probable that nature, when she brings forth the innumerable and manifold products of the organic kingdom by a wonderful combination of those few elements which are at her disposal, may likewise make use of these supposed extensive combining powers of the organic radicals, as the simplest means of accomplishing her greatest works.

We beg to express our warmest thanks to Dr. Lyon Playfair for the use of his laboratory and apparatus in carrying out the above investigation, and for the uniform kindness which we as his assistants have experienced at his hands.

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**XLV. Analysis of the Ashes of the Orange-Tree (Citrus aurantium). By Messrs. THOMAS H. ROWNEY and HENRY HOW\*.**

FOR the materials used in the following analyses we are indebted to the kindness of Mr. Da Cumara, who had sent it over for investigation from his plantations on the island of St. Michel, being desirous to become acquainted with the mineral constituents of the orange-tree, which forms the principal wealth of his country. The analyses were performed under the direction of Dr. Hofmann in the laboratory of the Royal College of Chemistry.

To prepare the ashes in a fit state for analysis, the different parts of the plant were heated in an inclined, open Hessian crucible, until the carbon was consumed†. The ashes thus obtained were mixed with a small quantity of oxide of mercury and ignited a second time in a platinum capsule over a spirit-lamp, in order to reproduce the sulphates, which in the former process had been reduced to sulphides.

\* Communicated by the Chemical Society; having been read April 5, 1847.

† To obtain the ash of the fruit, the oranges were cut into slices, and after separation of the seed dried on the sand-bath in a covered porcelain dish, and then burnt in a crucible.

The same quantity of ash served to determine the potash and soda, sulphuric and phosphoric acids, perphosphate of iron, lime and magnesia, silicic acid and accidental sand and charcoal. For this purpose, the hydrochloric acid solution was evaporated to dryness, gently ignited and extracted with hydrochloric acid. The solution thus obtained was divided into different parts. The first portion served for the determination of the potash and soda.

For this purpose the acids, lime, magnesia, &c. were removed by baryta, the excess of baryta by carbonate of ammonia, and the ammoniacal salts by gentle ignition. The residue, potash and soda, were estimated partly by separating them by means of bichloride of platinum (analyses of the ashes of the root and seed) and partly by the indirect method, namely, by converting the mixed chlorides into sulphates, weighing these and ascertaining the amount of sulphuric acid by means of chloride of barium (analyses of the stem, leaves and fruit).

In the second portion, sulphuric and phosphoric acids were determined, the former as sulphate of baryta, the latter by neutralizing the filtrate from the former with ammonia and precipitating the phosphoric acid by means of sesquichloride of iron and acetate of potash. This precipitate was dissolved in hydrochloric acid, a sufficient quantity of tartaric acid was added, and the phosphoric acid estimated in the form of pyrophosphate of magnesia, by precipitating with ammonia, chloride of ammonium and sulphate of magnesia. The latter precipitate, frequently containing a small quantity of iron, was redissolved in hydrochloric acid, and after the addition of some tartaric acid reprecipitated by ammonia. A third portion served for the estimation of perphosphate of iron, lime and magnesia. For this purpose the liquid was neutralized with ammonia, some acetate of potash was added, and the solution strongly acidulated with acetic acid, in order to keep the phosphate of lime, which might be precipitated, in solution; on heating perphosphate of iron subsides, from which the sesquioxide of iron was calculated according to the formula  $2\text{Fe}_2\text{O}_3 + 3\text{PO}_5$ . From the filtrate the lime was precipitated by means of oxalate of ammonia, and after the separation of the lime, the magnesia by means of phosphate of soda. Chlorine and carbonic acid were determined in separate portions of the ash. In this manner the following experimental numbers were obtained:—

	Roots.	Stem.	Leaves.	Fruit.	Seed.
	I. grms.	II. grms.	I. grms.	I. grms.	II. grms.
Quantity of ash employed for the general analysis .....	2.9360	3.07	1. grms. 3.2550 3.277	4.3040	4.653 3.7490
Whole amount of the hydro-chloric acid solution .....	164.634	154.059	1. grms. 229.956 139.376	202.696	171.503 207.520
Hydrochloric acid solution for the alkalies .....	21.320	33.05	23.226 22.94	28.913	20.422 20.716
Hydrochloric acid solution for sulphuric and phosphoric acids .....	24.989	35.442	39.393 27.456 16.18	23.616	22.574 33.013
Hydrochloric acid solution for lime, magnesia, &c. ..	31.959 25.686	39.155	38.506 36.693 25.827	26.331 21.550	22.324 27.356 21.716
Quantity of ash employed for the estimation of chlorine .....	1.4955	1.2235	1.1060	1.291	2.1230 1.927
Quantity of ash employed for the estimation of carbonic acid .....	.8400	.....	0.884	.....	1.5230 1.619
Quantity of the plant dried at 100° C. for the estimation of the amount of ash	1.7175	.....	1.1280	.....	1.7660 3.5450 .....
					1.3620 3.5415 1.3620 2.344 169.273 171.100 181.45 23.868 41.190 39.948 18.22 25.630 34.288 22.568 23.945 27.391 1.4595 .8270 0.6255 1.5275 0.585 ..... 3.7825

	Roots.	Stem.	Leaves.	Fruit.	Seed.
	I. grms.	II. grms.	I. grms.	II. grms.	I. grms.
Silicic acid .....	.0405	0.0445	.0330	0.0375	.0115
Sand and charcoal .....	.0125	0.0195	.0120	0.007 <sup>*</sup>	.0135
Mixed chlorides of potassium and sodium .....	.8185	0.846	.....	.....	.0140
Potassio-chloride of platinum .....	1.9089	.....	.....	.....	0.0225
Chloride of sodium .....	2.235	0.242	.....	.....	0.1325
Mixed sulphates of the alkalies .....	.....	.....	7772	0.784	0.0575
Sulphuric acid contained in the sulphates of the alkalies .....	.....	.....	3772	0.379	0.785
Sulphate of baryta for sulphuric acid .....	3946	0.42	3677	0.362	.7913
Pyrophosphate of magnesia for phosphoric acid .....	5007	0.53	7244	0.73	2.4861
Periphosphate of iron .....	0.566	0.588	0.358	0.0375	4.294
Carbonate of lime .....	2.1059	2.21	37565	2.69	0.0310
Pyrophosphate of magnesia for magnesia .....	.4454	0.47	.6675	0.469	.....
Chloride of silver .....	.0370	0.0275	.0055	0.008	.....
Carbonic acid .....	0.1600	.....	0.146	.....	.....
Amount of ash left on incineration .....	.0770	.....	.0310	.....	.....

These numbers correspond to the following percentage:—

*Analysis of the Ashes of the Root. Composition directly found.*

Amount of ashes left by 100 parts of the root . . . 4·48

	I.	II.	Mean.
Potash . . . . .	12·54	12·40	12·47
Soda . . . . .	3·72	3·57	3·64
Lime . . . . .	40·16	40·31	40·23
Magnesia . . . . .	5·55	5·60	5·57
Sesquioxide of iron	0·83	0·82	0·83
Chloride of sodium	1·01	0·91	0·95
Phosphoric acid .	10·80	10·93	10·86
Sulphuric acid .	4·61	4·76	4·68
Silicic acid . . .	1·38	1·45	1·42
Carbonic acid . .	19·04	19·04	19·04
Sand and charcoal	0·42	0·63	0·53
	100·06	100·37	100·22

Per-cent-age of the ash after deduction of the unessential constituents, carbonic acid, sand and charcoal:—

Potash . . . . .	15·43
Soda . . . . .	4·52
Lime . . . . .	49·89
Magnesia . . . . .	6·91
Sesquioxide of iron	1·02
Chloride of sodium	1·18
Phosphoric acid .	13·47
Sulphuric acid . .	5·78
Silicic acid . . .	1·75
	100·00

*Analysis of the Ashes of the Stem.*

Amount of ashes left by 100 parts of the stem . . . 2·74

	I.	II.	Mean.
Potash . . . . .	9·66	9·73	9·69
Soda . . . . .	2·61	2·47	2·54
Lime . . . . .	45·46	45·96	45·71
Magnesia . . . . .	5·28	5·24	5·26
Sesquioxide of iron	0·48	0·48	0·48
Chloride of sodium	0·19	0·24	0·21
Phosphoric acid .	14·18	14·17	14·17
Sulphuric acid . .	3·90	3·79	3·84
Silicic acid . . .	0·92	1·14	1·03
Carbonic acid . .	16·51	16·50	16·50
Sand and charcoal	0·33	0·21	0·27
	99·52	99·93	99·70
T 2			

Potash . . . . .	11·69
Soda . . . . .	3·07
Lime . . . . .	55·13
Magnesia . . . . .	6·34
Sesquioxide of iron	0·57
Chloride of sodium	0·25
Phosphoric acid . .	17·09
Sulphuric acid . .	4·64
Silicic acid . . . .	1·22
	<hr/>
	100·00

*Analysis of the Ashes of the Leaves.*

Amount of ashes left by 100 parts of the leaves . . 13·73

	I.	II.	Mean.
Potash . . . . .	12·87	12·48	12·67
Soda . . . . .	1·22	1·38	1·30
Lime . . . . .	43·32	43·44	43·38
Magnesia . . . . .	4·49	4·30	4·39
Sesquioxide of iron	0·36	0·44	0·40
Chloride of sodium	5·08	5·17	5·12
Phosphoric acid . .	2·46	2·58	2·52
Sulphuric acid . .	3·35	3·47	3·41
Silicic acid . . . .	3·67	3·78	3·72
Carbonic acid . . .	23·22	22·97	23·09
Sand and charcoal	0·24	0·21	0·23
	<hr/>	<hr/>	<hr/>
	100·28	100·22	100·23

Potash . . . . .	16·51
Soda . . . . .	1·68
Lime . . . . .	56·38
Magnesia . . . . .	5·72
Sesquioxide of iron	0·52
Chloride of sodium	6·66
Phosphoric acid . .	3·27
Sulphuric acid . .	4·43
Silicic acid . . . .	4·83
	<hr/>
	100·00

*Analysis of the Ashes of the Fruit.*

Amount of ashes left by 100 parts of the fruit . . .	3·94
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	I.	II.	Mean.
Potash . . . . .	28·21	28·32	28·26
Soda . . . . .	8·73	8·99	8·86
Lime . . . . .	19·20	18·83	19·02
Magnesia . . . . .	6·39	6·14	6·26
Sesquioxide of iron	0·35	0·36	0·35
Chloride of sodium	2·93	3·09	3·02
Phosphoric acid .	8·55	8·64	8·59
Sulphuric acid . .	2·88	2·93	2·90
Silicic acid . . .	0·31	0·38	0·34
Carbonic acid . .	20·38	20·22	20·30
Sand and charcoal	1·69	1·62	1·65
	99·62	99·52	99·55

Potash . . . . .	36·42
Soda . . . . .	11·42
Lime . . . . .	24·52
Magnesia . . . . .	8·06
Sesquioxide of iron	0·46
Chloride of sodium	3·87
Phosphoric acid . .	11·07
Sulphuric acid . .	3·74
Silicic acid . . . .	0·44
	100·00

*Analysis of the Ashes of the Seed.*

Amount of ashes left by 100 parts of the seed . . .	3·30
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	I.	II.	Mean.
Potash . . . . .	35·22	35·29	35·26
Soda . . . . .	0·77	0·84	0·81
Lime . . . . .	16·59	16·65	16·62
Magnesia . . . . .	7·87	7·51	7·69
Sesquioxide of iron	0·68	0·72	0·70
Chloride of sodium	0·77	0·67	0·72
Phosphoric acid . .	20·33	20·39	20·36
Sulphuric acid . .	4·46	4·48	4·47
Silicic acid . . . .	1·02	0·96	0·99
Carbonic acid . .	6·83	6·83	6·83
Sand and charcoal	5·76	5·78	5·77
	100·30	100·12	100·22

Potash . . . . .	40·28
Soda . . . . .	0·92
Lime . . . . .	18·97
Magnesia . . . . .	8·74
Sesquioxide of iron	0·80
Chloride of sodium	0·82
Phosphoric acid . .	23·24
Sulphuric acid . . .	5·10
Silicic acid . . . .	1·13—100·00

The preceding analyses furnish a new confirmation of the fact first observed by De Saussure, namely, that the largest amount of mineral constituents is deposited in those parts of the plant in which the process of assimilation appears to be most active. While the ash left by the root, stem, fruit and seed did not exceed from 3 to 4 per cent., the leaves left not less than 13 per cent. of fixed residue on incineration.

Regarding the composition of the different ashes, the great amount of carbonic acid found in the ashes of the root, the stem, and the fruit is at once obvious; proving that not only the fruit, but also the roots and stem, contain a large quantity of organic acids.

From the composition of the ashes of the root, the stem, and the leaves, the orange-tree belongs decidedly to the lime plants. In these three ashes the joint amount of lime and magnesia exceeds the quantity of the rest of the mineral constituents. In the ashes of the fruit and seed, however, the alkalies are as prevalent as they have been found in analogous cases. The amount of phosphoric acid (23·24) in the ash of the seed is considerable, as might be expected, still it is inferior to the quantities (34·81 and 42·02) which Mr. Souchay found on analysing the seeds of the citron (*Citrus Medica*) and quince-trees (*Pyrus Cydonia*). Nevertheless the ash of the orange-seed is very analogous in composition to the ashes of the last-mentioned seeds, as may be easily seen on comparing their analysis\*.

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XLVI. *On Quaternions; or on a New System of Imaginaries in Algebra.* By Sir WILLIAM ROWAN HAMILTON, LL.D., V.P.R.I.A., F.R.A.S., Corresponding Member of the Institute of France, &c., Andrews' Professor of Astronomy in the University of Dublin, and Royal Astronomer of Ireland.

[Continued from p. 219.]

37. **R**ESUMING now the quaternion form of the equation of the ellipsoid,

$$(\alpha\rho + \rho\alpha)^2 - (\beta\rho - \rho\beta)^2 = 1, \dots \quad (1.)$$

\* Liebig's Annals, liv. p. 343.

and making

$$\alpha + \beta = \frac{\iota}{\iota^2 - \kappa^2}, \quad \alpha - \beta = \frac{\kappa}{\iota^2 - \kappa^2}, \quad \dots \quad (2.)$$

and

$$\frac{\iota\rho + \rho\kappa}{\iota^2 - \kappa^2} = Q, \quad \frac{\rho\iota + \kappa\rho}{\iota^2 - \kappa^2} = Q', \quad \dots \quad (3.)$$

the two linear factors of the first member of the equation (1.) become the two conjugate quaternions  $Q$  and  $Q'$ , so that the equation itself becomes

$$QQ' = 1. \quad \dots \quad (4.)$$

But by articles 19 and 20 (Phil. Mag. for July 1846), the product of any two conjugate quaternions is equal to the square of their common tensor; this common tensor of the two quaternions  $Q$  and  $Q'$  is therefore equal to unity. Using, therefore, as in those articles, the letter  $T$  as the characteristic of the operation of *taking the tensor* of a quaternion, the equation of the ellipsoid reduces itself to the form

$$TQ = 1; \quad \dots \quad (5.)$$

or, substituting for  $Q$  its expression (3.),

$$T \left( \frac{\iota\rho + \rho\kappa}{\iota^2 - \kappa^2} \right) = 1; \quad \dots \quad (6.)$$

which latter form might also have been obtained, by the substitutions (2.), from the equation (3.) of the 30th article (Phil. Mag., June 1847), namely from the following\*:

$$T(\alpha\rho + \rho\alpha + \beta\rho - \rho\beta) = 1. \quad \dots \quad (7.)$$

38. In the geometrical construction or generation of the ellipsoid, which was assigned in the preceding articles of this paper (see the Numbers of the Philosophical Magazine for June and September 1847), the significations of some of the recent symbols are the following. The two constant vectors  $\iota$  and  $\kappa$  may be regarded as denoting, respectively, (in lengths and in directions,) the two sides of the generating triangle  $ABC$ , which are drawn from the centre  $c$  of the auxiliary and diacentric sphere, to the fixed superficial point  $B$  of the ellipsoid, and to the centre  $A$  of the same ellipsoid; the third side of the triangle, or the vector from  $A$  to  $B$ , being therefore denoted (in length and in direction) by  $\iota - \kappa$ : while  $\rho$  is the radius vector of the ellipsoid, drawn from the centre  $A$  to a

\* See equation (35.) of the Abstract in the Proceedings of the Royal Irish Academy for July 1846. The equation of the ellipsoid marked (1.) in article 37 of the present paper, was communicated to the Academy in December 1845, and is numbered (21.) in the Proceedings of that date.

variable point  $\mathbf{E}$  of the surface; so that the constant vector  $\mathbf{i} - \mathbf{x}$  is, by the construction, a particular value of this variable vector  $\rho$ . The vector from  $A$  to  $C$ , being the opposite of that from  $C$  to  $A$ , is denoted by  $-\mathbf{x}$ ; and if  $D$  be still the same auxiliary point on the surface of the auxiliary sphere, which was denoted by the same letter in the account already printed of the construction, then the vector from  $C$  to  $D$ , which may be regarded as being (in a sense to be hereafter more fully considered) the *reflexion* of  $-\mathbf{x}$  with respect to  $\rho$ , is  $= -\rho\mathbf{x}\rho^{-1}$ ; and consequently the vector from  $D$  to  $B$  is  $= \mathbf{i} + \rho\mathbf{x}\rho^{-1}$ . The lengths of the two straight lines  $BD$ , and  $AE$ , are therefore respectively denoted by the two tensors,  $T(\mathbf{i} + \rho\mathbf{x}\rho^{-1})$  and  $T\rho$ ; and the rectangle under those two lines is represented by the product of these two tensors, that is by the tensor of the product, or by  $T(\mathbf{i}\rho + \rho\mathbf{x})$ . But by the fundamental equality of the lengths of the diagonals,  $AE$ ,  $BD'$ , of the plane quadrilateral  $ABED'$  in the construction, this rectangle under  $BD$  and  $AE$  is equal to the constant rectangle under  $BD$  and  $BD'$ , that is under the whole secant and its external part, or to the square on the tangent from  $B$ , if the point  $B$  be supposed external to the auxiliary sphere, which has its centre at  $C$ , and passes through  $D$ ,  $D'$ , and  $A$ . Thus  $T(\mathbf{i}\rho + \rho\mathbf{x})$  is equal to  $(T\mathbf{i})^2 - (Tx)^2$ , or to  $\mathbf{x}^2 - \mathbf{i}^2$ , which difference is here a positive scalar, because it is supposed that  $CB$  is longer than  $CA$ , or that

$$T\mathbf{i} > Tx; \quad \dots \dots \dots \quad (8.)$$

and the quaternion equation (6.) of the ellipsoid reproduces itself, as a result of the geometrical construction, under the slightly simplified form \*

$$T(\mathbf{i}\rho + \rho\mathbf{x}) = \mathbf{x}^2 - \mathbf{i}^2. \quad \dots \dots \dots \quad (9.)$$

And to verify that this equation relative to  $\rho$  is satisfied (as we have seen that it ought to be) by the particular value

$$\rho = \mathbf{i} - \mathbf{x}, \quad \dots \dots \dots \quad (10.)$$

which corresponds to the particular position  $B$  of the variable point  $\mathbf{E}$  on the surface of the ellipsoid, we have only to observe that, identically,

$$\begin{aligned} \mathbf{i}(\mathbf{i} - \mathbf{x}) + (\mathbf{i} - \mathbf{x})\mathbf{x} &= \mathbf{i}^2 - \mathbf{i}\mathbf{x} + \mathbf{i}\mathbf{x} - \mathbf{x}^2 \\ &= \mathbf{i}^2 - \mathbf{x}^2 = -(\mathbf{x}^2 - \mathbf{i}^2); \end{aligned}$$

and that (by article 19) the tensor of a negative scalar is equal to the positive opposite thereof.

39. The foregoing article contains a sufficiently simple

\* See the Proceedings of the Royal Irish Academy for July 1846, equation (44.).

process for the *retranslation* of the geometrical construction\* of the ellipsoid described in article 31, into the language of the calculus of quaternions, from which the construction itself had been originally derived, in the manner stated in the 30th article of this paper. Yet it may not seem obvious to readers unfamiliar with this calculus, why the expression  $-\rho x \rho^{-1}$  was taken, in that foregoing article 38, as one denoting, in length and in direction, that radius of the auxiliary sphere which was drawn from  $c$  to  $d$ ; nor in what sense, and for what reason, this expression  $-\rho x \rho^{-1}$  has been said to represent the reflexion of the vector  $-x$  with respect to  $\rho$ . As a perfectly clear answer to each of these questions, or a distinct justification of each of the assumptions or assertions thus referred to, may not only be useful in connection with the present mode of considering the ellipsoid, but also may throw light on other applications of quaternions to the treatment of geometrical and physical problems, we shall not think it an irrelevant digression to enter here into some details respecting this expression  $-\rho x \rho^{-1}$ , and respecting the ways in which it may present itself in calculations such as the foregoing. Let us therefore now denote by  $\sigma$  the vector, whatever it may be, from  $c$  to  $d$  in the construction ( $c$  being still the centre of the sphere); and let us propose to find an expression for this sought vector  $\sigma$ , as a function of  $\rho$  and of  $x$ , by the principles of the calculus of quaternions.

40. For this purpose we have first the equation between tensors,

$$T\sigma = Tx; \quad \dots \quad (11.)$$

which expresses that the two vectors  $\sigma$  and  $x$  are equally long, as being both radii of one common auxiliary sphere, namely those drawn from the centre  $c$  to the points  $d$  and  $a$ . And secondly, we have the equation

$$V \cdot (\sigma - x) \rho = 0, \quad \dots \quad (12.)$$

where  $V$  is the characteristic of the operation of *taking the vector* of a quaternion; which equation expresses immediately that the product of the two vectors  $\sigma - x$  and  $\rho$  is scalar, and

\* The brevity and novelty of this rule for constructing that important surface may perhaps justify the reprinting it here. It was as follows: From a fixed point  $a$  on the surface of a sphere, draw a variable chord  $ad$ ; let  $d'$  be the second point of intersection of the spheric surface with the secant  $bd$ , drawn to the variable extremity  $d$  of this chord  $ad$  from a fixed external point  $b$ ; take the radius vector  $ae$  equal in length to  $bd'$ , and in direction either coincident with, or opposite to, the chord  $ad$ ; the locus of the point  $e$ , thus constructed, will be an ellipsoid, which will pass through the point  $b$  (and will have its centre at  $a$ ). See Proceedings of the Royal Irish Academy for July 1846.

therefore that these two vector-factors are either exactly similar or exactly opposite in direction; since otherwise their product would be a quaternion, having always a vector part, although the scalar part of this quaternion-product  $(\sigma - \mathbf{x})\rho$  might vanish, namely by the factors becoming perpendicular to each other. Such being the immediate and general significance of the equation (12.), the justification of our establishing it in the present question is derived from the consideration that the radius vector  $\rho$ , drawn from the centre  $A$  to the surface  $E$  of the ellipsoid, has, by the construction, a direction either exactly similar or exactly opposite to the direction of that *guide-chord* of the auxiliary sphere which is drawn from  $A$  to  $D$ , that is, from the end of the radius denoted by  $\mathbf{x}$  to the end of the radius denoted by  $\sigma$ . For, that the chord so drawn is properly denoted, in length and in direction, by the symbol  $\sigma - \mathbf{x}$ , follows from principles respecting *addition and subtraction of directed lines*, which are indeed *essential*, but are *not peculiar*, to the geometrical applications of quaternions; had occurred, in various ways, to several independent inquirers, before quaternions (as *products or quotients of directed lines in space*) were thought of; and are now extensively received.

41. The two equations (11.) and (12.) are evidently both satisfied when we suppose  $\sigma = \mathbf{x}$ ; but because the point  $D$  is in general different from  $A$ , we must endeavour to find another value of the vector  $\sigma$ , distinct from  $\mathbf{x}$ , which shall satisfy the same two equations. Such a value, or expression, for this sought vector  $\sigma$  may be found at once, so far as the equation (12.) is concerned, by observing that, in virtue of this latter equation,  $\sigma - \mathbf{x}$  must bear some scalar ratio to  $\rho$ , or must be equal to this vector  $\rho$  multiplied by some scalar coefficient  $x$ , so that we may write

$$\sigma = \mathbf{x} + x\rho; \dots \quad (13.)$$

and then, on substituting this expression for  $\sigma$  in the former equation (11.), we find that  $x$  must satisfy the condition

$$T(\mathbf{x} + x\rho) = T\mathbf{x}, \dots \quad (14.)$$

in which this sought coefficient  $x$  is supposed to be some scalar different from zero, that is, in other words, some positive or negative number. Squaring both members of this last condition, and observing that by article 19 the square of the tensor of a vector is equal to the negative of the square of that vector, we find the new equation

$$-(\mathbf{x} + x\rho)^2 = -\mathbf{x}^2. \dots \quad (15.)$$

But also, generally, if  $\mathbf{x}$  and  $\rho$  be vectors and  $x$  a scalar,

$$(\mathbf{x} + x\rho)^2 = \mathbf{x}^2 + x(x\rho + \rho\mathbf{x}) + x^2\rho^2;$$

adding therefore  $x^2$  to both members of (15.), dividing by  $-x$ , and then eliminating  $x$  by (13.), which is done by merely changing  $x\rho + x\rho^2$  to  $\sigma\rho$ , we find the equation

$$\sigma\rho + \rho x = 0; \quad \dots \dots \dots \quad (16.)$$

and finally

$$\sigma = -\rho x \rho^{-1}; \quad \dots \dots \dots \quad (17.)$$

so that the expression already assigned for the vector from  $c$  to  $d$ , presents itself as the result of this analysis. And in fact the tensor of this expression (17.) is equal to  $Tx$ , by the general rule for the tensor of a product, or because  $(-\rho x \rho^{-1})^2 = \rho x \rho^{-1} \rho x \rho^{-1} = \rho x^2 \rho^{-1} = x^2$ , since  $x^2$  is a (negative) scalar; while the product  $(\sigma - x)\rho$ , being  $= -(x\rho + \rho x)$ , is equal, by article 20, to an expression of scalar form.

42. Conversely if, in any investigation conducted on the present principles, we meet with the expression  $-\rho x \rho^{-1}$ , we may perceive in the way just now mentioned, that it denotes a vector of which the square is equal to that of  $x$ ; and that, if  $x$  be subtracted from it, the remainder gives a scalar product when it is multiplied into  $\rho$ : so that, if we denote this expression by  $\sigma$ , or establish the equation (17.), the equations (11.) and (12.) will then be satisfied, and the vector  $\sigma$  will have the same length as  $x$ , while the directions of  $\sigma - x$  and  $\rho$  will be either exactly similar or exactly opposite to each other. We may therefore be thus led to regard, subject to this condition (17.) or (16.), the two vector-symbols  $\sigma$  and  $x$  as denoting, in length and in direction, two radii of one common sphere, such that the chord-line  $\sigma - x$  connecting their extremities has the direction of the line  $\rho$ , or of that line reversed. Hence also, by the elementary property of a plane isosceles triangle, we may see that, under the same condition, the inclination of  $\sigma$  to  $\rho$  is equal to the inclination of  $x$  to  $-\rho$ , or of  $-x$  to  $\rho$ ; in such a manner that the bisector of the external vertical angle of the isosceles triangle, or the bisector of the angle at the centre of the sphere between the two radii  $\sigma$  and  $-x$ , is a new radius parallel to  $\rho$ , because it is parallel to the base of the triangle (ACD), or to the chord (AD) just now mentioned. And by conceiving a diameter of the sphere parallel to this chord, or to  $\rho$ , and supposing  $-x$  to denote that reversed radius which coincides in situation with the radius  $x$ , but is drawn from the surface to the centre (that is, in the recent construction, from  $a$  to  $c$ ), while  $\sigma$  is still drawn from centre to surface (from  $c$  to  $d$ ), we may be led to regard  $\sigma$ , or  $-\rho x \rho^{-1}$ , as the *reflexion* of  $-x$  with respect to the diameter parallel to  $\rho$ , or simply with respect to  $\rho$  itself, as was remarked in the 38th article; since the vector-symbols  $\rho$ ,  $\sigma$ , &c. are supposed,

in these calculations, to indicate indeed the *lengths and directions*, but not the situations, of the straight lines which they are employed to denote.

43. The same geometrical interpretation of the symbol  $-\rho x \rho^{-1}$  may be obtained in several other ways, among which we shall specify the following. Whatever the lengths and directions of the two straight lines denoted by  $\rho$  and  $x$  may be, we may always conceive that the latter line, regarded as a vector, is or may be decomposed, by two different projections, into two partial or component vectors,  $x'$  and  $x''$ , of which one is parallel and the other is perpendicular to  $\rho$ ; so that they satisfy respectively the equations of parallelism and perpendicularity (see article 21), and that we have consequently,

$$x = x' + x''; \quad V.x'\rho = 0; \quad S.x''\rho = 0; \quad \dots \quad (18.)$$

where  $S$  is the characteristic of the operation of *taking the scalar* of a quaternion. The equation of parallelism gives  $\rho x' = x'\rho$ , and the equation of perpendicularity gives  $\rho x'' = -x''\rho$ ; hence the proposed expression  $-\rho x \rho^{-1}$  resolves itself into the two parts,

$$\begin{aligned} -\rho x' \rho^{-1} &= -x' \rho \rho^{-1} = -x'; \\ -\rho x'' \rho^{-1} &= +x'' \rho \rho^{-1} = +x''; \end{aligned} \quad \dots \quad (19.)$$

so that we have, upon the whole,

$$-\rho x \rho^{-1} = -\rho(x' + x'')\rho^{-1} = -x' + x''. \quad \dots \quad (20.)$$

The part  $-x'$  of this last expression, which is parallel to  $\rho$ , is the same as the corresponding part of  $-x$ ; but the part  $+x''$ , perpendicular to  $\rho$ , is the same with the corresponding part of  $+x$ , or is opposite to the corresponding part of  $-x$ ; we may therefore be led by this process also to regard the expression (17.) as denoting the reflexion of the vector  $-x$ , with respect to the vector  $\rho$ , regarded as a reflecting line; and we see that the direction of  $\rho$ , or that of  $-\rho$ , is exactly intermediate between the two directions of  $-x$  and  $-\rho x \rho^{-1}$ , or between those of  $x$  and of  $\rho x \rho^{-1}$ .

44. The equation (9.) of the ellipsoid, in article 38, or the equation (4.) in article 37, may be more fully written thus:

$$(i\rho + \rho x)(\rho i + x\rho) = (x^2 - i^2)^2. \quad \dots \quad (21.)$$

And to express that we propose to cut this surface by any diametral plane, we may write the equation

$$\varpi\rho + \rho\varpi = 0, \quad \dots \quad (22.)$$

where  $\varpi$  denotes a vector to which that cutting plane is perpendicular: thus, if in particular, we change  $\varpi$  to  $x$ , we find, for the corresponding plane through the centre, the equation

$$\imath\rho + \rho\mathbf{x} = 0, \quad \dots \quad \dots \quad \dots \quad \dots \quad (23.)$$

which, when combined with (21.), gives

$$(\mathbf{x}^2 - \mathbf{i}^2)^2 = (\mathbf{i} - \mathbf{x})\rho \cdot \rho(\mathbf{i} - \mathbf{x}) = (\mathbf{i} - \mathbf{x})\rho^2(\mathbf{i} - \mathbf{x}) = (\mathbf{i} - \mathbf{x})^2\rho^2,$$

that is,

$$\rho^2 = \left( \frac{\mathbf{x}^2 - \mathbf{i}^2}{\mathbf{i} - \mathbf{x}} \right)^2; \quad \dots \quad \dots \quad \dots \quad \dots \quad (24.)$$

but this is the equation of a sphere concentric with the ellipsoid; therefore the diametral plane (23.) cuts the ellipsoid in a *circle*, or the plane itself is a *cyclic plane*. We see also that the vector  $\mathbf{x}$ , as being perpendicular to this plane (23.), is one of the *cyclic normals*, or normals to planes of circular section; which agrees with the construction, since we saw, in article 36, that the auxiliary or diacentric sphere, with centre  $\mathbf{c}$ , touches one cyclic plane at the centre  $\mathbf{A}$  of the ellipsoid. The same construction shows that the other cyclic plane ought to be perpendicular to the vector  $\mathbf{i}$ ; and accordingly the equation

$$\imath\rho + \rho\imath = 0 \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (25.)$$

represents this second cyclic plane; for, when combined with the equation (21.) of the ellipsoid, it gives

$$(\mathbf{x}^2 - \mathbf{i}^2)^2 = \rho(\mathbf{x} - \mathbf{i}) \cdot (\mathbf{x} - \mathbf{i})\rho = \rho(\mathbf{x} - \mathbf{i})^2\rho = (\mathbf{x} - \mathbf{i})^2\rho^2,$$

and therefore conducts to the same equation (24.) of a concentric sphere as before; which sphere (24.) is thus seen to contain the intersection of the ellipsoid (21.) with the plane (25.), as well as that with the plane (23.). If we use the form (9.), we have only to observe that whether we change  $\rho\mathbf{x}$  to  $-\mathbf{x}\rho$ , or  $\imath\rho$  to  $-\rho\imath$ , we are conducted in each case to the following expression for the length of the radius vector of the ellipsoid, which agrees with the equation (24.):

$$T\rho = \frac{\mathbf{x}^2 - \mathbf{i}^2}{T(\mathbf{i} - \mathbf{x})}. \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (26.)$$

And because  $\mathbf{x}^2 - \mathbf{i}^2$  denotes the square upon the tangent drawn to the auxiliary sphere from the external point  $\mathbf{B}$ , while  $T(\mathbf{i} - \mathbf{x})$  denotes the length of the side  $\mathbf{BA}$  of the generating triangle, we see by this easy calculation with quaternions, as well as by the more purely geometrical reasoning which was alluded to, and partly stated, in the 36th article, that the common radius of the two diametral and circular sections of the ellipsoid is equal to the straight line which was there called  $\mathbf{BG}$ , and which had the direction of  $\mathbf{BA}$ , while terminating, like it, on the surface of the auxiliary sphere; so that the two last lines  $\mathbf{BA}$ , and  $\mathbf{BG}$ , were connected with that sphere and with each other, in this or in the opposite order, as the whole se-

cant and the external part. In fact, as the point  $D$ , in the construction approaches, in any direction, on the surface of the auxiliary sphere, to  $A$ , the point  $D'$  approaches to  $G$ ; and  $BD'$ , and therefore also  $AE$ , tends to become equal in length to  $BG$ ; while the direction of  $AE$ , being the same with that of  $AD$ , or opposite thereto, tends to become tangential to the sphere, or perpendicular to  $AC$ : the line  $BG$  is therefore equal to the radius of that diametral and circular section of the ellipsoid which is made by the plane that touches the auxiliary sphere at  $A$ . And again, if we conceive the point  $D'$  to revolve on the surface of the sphere from  $G$  to  $G$  again, in a plane perpendicular to  $BC$ , then the lines  $AD$  and  $AE$  will revolve together in another plane parallel to that last mentioned, and perpendicular likewise to  $BC$ ; while the length of  $AE$  will be still equal to the same constant line  $BG$  as before: which line is therefore found to be equal to the common radius of both the diametral and circular sections of the ellipsoid, whether as determined by the geometrical construction which the calculus of quaternions suggested, or immediately by that calculus itself.

45. We may write the equation (21.) of the ellipsoid as follows:

$$f(\rho) = 1, \quad \dots \quad \dots \quad \dots \quad \dots \quad (27.)$$

if we introduce a scalar function  $f$  of the variable vector  $\rho$ , defined as follows:

$$(x^2 - i^2)^2 f(\rho) = (i\rho + \rho x)(\rho i + x\rho) = i\rho^2 i + i\rho x\rho + \rho x\rho i + \rho x^2 \rho;$$

or thus, in virtue of article 20,

$$(x^2 - i^2)^2 f(\rho) = (i^2 + x^2)\rho^2 + 2S.i\rho x\rho. \quad \dots \quad (28.)$$

Let  $\rho + \tau$  denote another vector from the centre to the surface of the same ellipsoid; we shall have, in like manner,

$$f(\rho + \tau) = 1, \quad \dots \quad \dots \quad \dots \quad \dots \quad (29.)$$

where

$$f(\rho + \tau) = f(\rho) + 2S.\tau\rho + f(\tau), \quad \dots \quad \dots \quad \dots \quad \dots \quad (30.)$$

if we introduce a new vector symbol  $v$ , defined by the equation

$$(x^2 - i^2)^2 v = (i^2 + x^2)\rho + i\rho x + x\rho i; \quad \dots \quad \dots \quad \dots \quad \dots \quad (31.)$$

because generally, for any two vectors  $\rho$  and  $\tau$ ,

$$(\rho + \tau)^2 = \rho^2 + 2S.\rho\tau + \tau^2, \quad \dots \quad \dots \quad \dots \quad \dots \quad (32.)$$

and, for any four vectors,  $i, x, \rho, \tau$ ,

$$S.i\tau x\rho = S.\tau x\rho i = S.x\rho i\tau = S.\rho i\tau x; \quad \dots \quad \dots \quad \dots \quad \dots \quad (33.)$$

which last principle, respecting certain transpositions of vector symbols, as factors of a product under the sign  $S.$ , shows,

when combined with the equations (27.), (28.), and (31.), that we have also this simple relation :

$$S \cdot v\rho = 1. \quad \dots \dots \dots \quad (34.)$$

Subtracting (27.) from (29.), attending to (30.), changing  $\tau$  to  $T\tau$ .  $U\tau$ , where  $U$  is, as in article 19, the characteristic of the operation of *taking the versor* of a quaternion (or of a vector), and dividing by  $T\tau$ , we find :

$$0 = \frac{f(\rho + \tau) - f(\rho)}{T\tau} = 2S \cdot vU\tau + T\tau \cdot f(U\tau). \quad (35.)$$

This is a rigorous equation, connecting the *length* or the *tensor*  $T\tau$ , of any chord  $\tau$  of the ellipsoid, drawn from the extremity of the semidiameter  $\rho$ , with the *direction* of that chord  $\tau$ , or with the *versor*  $U\tau$ ; it is therefore only a new form of the equation of the ellipsoid itself, with the origin of vectors removed from the centre to a point upon the surface. If we now conceive the chord  $\tau$  to diminish in length, the term  $T\tau \cdot f(U\tau)$  of the right-hand member of this equation (35.) tends to become  $= 0$ , on account of the factor  $T\tau$ ; and therefore the other term  $2S \cdot vU\tau$  of the same member must tend to the same limit zero. In this way we arrive easily at an equation expressing the *ultimate law of the directions of the evanescent chords* of the ellipsoid, at the extremity of any given or assumed semidiameter  $\rho$ ; which equation is  $0 = 2S \cdot vU\tau$ , or simply,

$$0 = S \cdot v\tau, \quad \dots \dots \dots \quad (36.)$$

if  $\tau$  be a tangential vector. The vector  $v$  is therefore perpendicular to all such tangents, or infinitesimal chords of the ellipsoid, at the extremity of the semidiameter  $\rho$ ; and consequently it has the direction of the *normal* to that surface, at the extremity of that semidiameter. The *tangent plane* to the same surface at the same point is represented by the equation (34.), if we treat, therein, the normal vector  $v$  as constant, and if we regard the symbol  $\rho$  as denoting, in the same equation (34.), a variable vector, drawn from the centre of the ellipsoid to any point upon that tangent plane. This equation (34.) of the tangent plane may be written as follows:

$$S \cdot v(\rho - v^{-1}) = 0; \quad \dots \dots \dots \quad (37.)$$

and under this form it shows easily that the symbol  $v^{-1}$  represents, in length and in direction, the perpendicular let fall from the origin of the vectors  $\rho$ , that is from the centre of the ellipsoid, upon the plane which is thus represented by the equation (34.) or (37.); so that the vector  $v$  itself, as determined by the equation (31.), may be called the *vector of proximity*.

mity\* of the tangent plane of the ellipsoid, or of an element of that surface, to the centre, at the end of that semidiameter  $\rho$  from which  $\nu$  is deduced by that equation.

46. Conceive now that at the extremity of an infinitesimal chord  $d\rho$  or  $\tau$ , we draw another normal to the ellipsoid; the expression for any arbitrary point on the former normal, that is the symbol for the vector of this point, drawn from the centre of the ellipsoid, or from the origin of the vectors  $\rho$ , is of the form  $\rho + nv$ , where  $n$  is an arbitrary scalar; and in like manner the corresponding expression for an arbitrary point on the latter and infinitely near normal, or for its vector from the same centre of the ellipsoid, is  $\rho + d\rho + (n + dn)(\nu + dv)$ , where  $dn$  is an arbitrary but infinitesimal scalar, and  $dv$  is the differential of the vector of proximity  $\nu$ , which may be found as a function of the differential  $d\rho$  by differentiating the equation (31.), which connects the two vectors  $\nu$  and  $\rho$  themselves. In this manner we find, from (31.),

$$(x^2 - i^2)^2 dv = (i^2 + x^2) d\rho + id\rho x + x d\rho i; \dots \quad (38.)$$

and the condition required for the intersection of the two near normals, or for the existence of a point common to both, is expressed by the formula

$$\rho + d\rho + (n + dn)(\nu + dv) = \rho + nv; \dots \quad (39.)$$

which may be more concisely written as follows:

$$d\rho + d.nv = 0; \dots \quad (40.)$$

or thus :

$$d\rho + ndv + dn\nu = 0. \dots \quad (41.)$$

We can eliminate the two scalar coefficients,  $n$  and  $dn$ , from this last equation, according to the rules of the calculus of quaternions, by the method exemplified in the 24th article of this paper (Phil. Mag., August 1846), or by operating with the characteristic  $S.\nu dv$ , because generally

$$S.\nu\mu^2 = 0, \quad S.\nu\mu\nu = 0,$$

whatever vectors  $\mu$  and  $\nu$  may be; so that here,

$$S.\nu dv ndv = 0, \quad S.\nu dv dn\nu = 0.$$

\* This name, "vector of proximity," was suggested to the writer by a phraseology of Sir John Herschel's; and the equation (31.), of article 45, which determines this vector for the ellipsoid, was one of a few equations which were designed to have been exhibited to the British Association at its meeting in 1846: but were accidentally forwarded at the last moment to Collingwood, instead of Southampton, and did not come to the hands of the eminent philosopher just mentioned, until it was too late for him to do more than return the paper, with some of those encouraging expressions by which he delights to cheer, as opportunities present themselves, all persons whom he conceives to be labouring usefully for science.

In this manner we find from (41.) the following very simple formula:  $S.vdvdp=0; \dots \dots \dots$  (42.)

which is easily seen, on the same principles, to hold good, as the *quaternion form of the differential equation of the lines of curvature on a curved surface generally*, if  $v$  be still the *vector of proximity of the superficial element* of the curved surface to the origin of the vectors  $\rho$ , which vector  $v$  is determined by the general condition  $S.vd\rho=0, \dots \dots \dots$  (43.) combined with the equation already written,

$$S.v\rho=1 \quad (34.);$$

or simply if  $v$  be a *normal vector*, satisfying the condition (43.) alone. Substituting, therefore, in the case of the ellipsoid, the expression for  $dv$  given by (38.), and observing that  $S.vdp^2=0$ , we find that we may write the equation of the lines of curvature for this particular surface as follows:

$$S.v(id\rho x + xd\rho i)dp=0; \dots \dots \dots \quad (44.)$$

which equation, when treated by the rules of the present calculus, admits of being in many ways symbolically transformed, and may also, with little difficulty, be translated into geometrical enunciations.

47. Thus if we observe that, by article 20,  $i\tau x - x\tau i$  is a *scalar form*, whatever three vectors may be denoted by  $i, x, \tau$ ; and if we attend to the equation (43.), which expresses that the normal  $v$  is perpendicular to the linear element, or infinitesimal chord,  $d\rho$ ; we shall perceive that, for *every* direction of that element, the following equation holds good:

$$S.v(id\rho x - x\tau i)dp=0. \dots \dots \dots \quad (45.)$$

We have therefore, from (44.), for those *particular* directions which belong to the lines of curvature, this simplified equation;

$$S.vdpxd\rho=0; \dots \dots \dots \quad (46.)$$

which may be still a little abridged, by writing instead of  $d\rho$  the symbol  $\tau$  of a tangential vector, already used in (36.); for thus we obtain the formula:

$$S.vi\tau x\tau=0. \dots \dots \dots \quad (47.)$$

We might also have observed that by the same article 20 (Phil. Mag., July 1846),  $i\tau x + x\tau i$  and therefore  $id\rho x + xd\rho i$  is a *vector form*, and that by article 26 (Phil. Mag., August 1846), three vector-factors under the characteristic  $S$  may be in any manner transposed, with only a change (at most) in the positive or negative sign of the resulting scalar; from which it would have followed, by a process exactly similar to the foregoing, that the equation (44.) of the lines of curvature on an ellipsoid may be thus written,

$$S.vd\rho id\rho x=0; \dots \dots \dots \quad (48.)$$

or, substituting for the linear element  $d\rho$  the tangential vector  $\tau$ ,

$$S \cdot \nu \tau i \tau x = 0; \quad \dots \dots \dots \quad (49.)$$

or finally, by the principles of the same 20th article,

$$\nu \tau i \tau x - x \tau i \tau v = 0. \quad \dots \dots \dots \quad (50.)$$

48. Under this last form, it was one of a few equations selected in September 1846, for the purpose of being exhibited to the Mathematical Section of the British Association at Southampton ; although it happened\* that the paper containing those equations did not reach its destination in time to be so exhibited. The equations here marked (49.) and (50.) were however published before the close of the year in which that meeting was held, as part of the abstract of a communication which had been made to the Royal Irish Academy in the summer of that year. (See the Proceedings of the Academy for July 1846, equations (46.) and (47.).) From the somewhat discursive character of the present series of communications on Quaternions, and from the desire which the author feels to render them, to some extent, complete within themselves, or at least intelligible to those mathematical readers of the Philosophical Magazine who may be disposed to favour him with their attention, to the degree which the novelty of the conceptions and method may require, without its being necessary for such readers to refer to other publications of his own, he is induced, and believes himself to be authorized, to copy here a few other equations from that short and hitherto unpublished Southampton paper, and to annex to them another formula which may be found in the Proceedings, already cited, of the Royal Irish Academy : together with a more extensive formula, which he believes to be new.

49. Besides the equation of the ellipsoid,

$$(i\rho + \rho x)(\rho i + x\rho) = (x^2 - i^2)^2 \quad (21.), \text{ art. 44};$$

with the expression derived from it, for the vector of proximity of that surface to its centre,

$$(x^2 - i^2)^2 \nu = (i^2 + x^2)\rho + i\rho x + x\rho i \quad (31.), \text{ art. 45};$$

the equation for the lines of curvature on the ellipsoid,

$$\nu \tau i \tau x - x \tau i \tau v = 0 \quad (50.), \text{ art. 47};$$

and the equation  $\nu \tau + \tau \nu = 0, \quad \dots \dots \dots \quad (51.)$

which is a form of the relation  $S \cdot \nu \tau = 0$ , that is of the equation (36.), article 45, of the present series of communications ; the author gave, in the paper which has been above referred to, the following symbolic transformation, for the well-known characteristic of operation,

$$\left( \frac{d}{dx} \right)^2 + \left( \frac{d}{dy} \right)^2 + \left( \frac{d}{dz} \right)^2,$$

\* See the note to article 45.

which seems to him to open a wide and new field of analytical research, connected with many important and difficult departments of the mathematical study of nature.

A QUATERNION, *symbolically considered*, being (according to the views originally proposed by the author in 1843) an algebraical quadrinomial of the form  $w+ix+jy+kz$ , where  $wxyz$  are any four real numbers (positive or negative or zero), while  $ijk$  are three co-ordinate imaginary units, subject to the fundamental laws of combination (see Phil. Mag. for July 1844):

$$\left. \begin{array}{l} i^2=j^2=k^2=-1; \\ ij=k; jk=i; ki=j; \\ ji=-k; kj=-i; ik=-j; \end{array} \right\} \dots \quad (a.)$$

it results at once from these definitions, or laws of symbolic combination, (a.), that if we introduce a new characteristic of operation,  $\triangleleft$ , defined with relation to these three symbols  $ijk$ , and to the known operation of partial differentiation, performed with respect to three independent but real variables  $xyz$ , as follows:

$$\triangleleft = \frac{id}{dx} + \frac{jd}{dy} + \frac{kd}{dz}; \quad \dots \quad (b.)$$

this new characteristic  $\triangleleft$  will have the negative of its symbolic square expressed by the following formula:

$$-\triangleleft^2 = \left( \frac{d}{dx} \right)^2 + \left( \frac{d}{dy} \right)^2 + \left( \frac{d}{dz} \right)^2; \quad \dots \quad (c.)$$

of which it is clear that the applications to analytical physics must be extensive in a high degree. In the paper\* designed for Southampton it was remarked, as an illustration, that this result enables us to put the known thermological equation,

$$\frac{d^2v}{dx^2} + \frac{d^2v}{dy^2} + \frac{d^2v}{dz^2} + a \frac{dv}{dt} = 0,$$

under the new and more symbolic form,

$$\left( \triangleleft^2 - \frac{ad}{dt} \right) v = 0; \quad \dots \quad (d.)$$

while  $\triangleleft v$  denotes, in quantity and in direction, the *flux* of heat, at the time  $t$  and at the point  $xyz$ .

50. In the Proceedings of the Royal Irish Academy for July 1846, it will be found to have been noticed that the same new characteristic  $\triangleleft$  gives also this other general transformation, perhaps not less remarkable, nor having less extensive

\* In that paper itself, the characteristic was written  $\nabla$ ; but this more common sign has been so often used with other meanings, that it seems desirable to abstain from appropriating it to the new signification here proposed.

consequences, and which presents itself under the form of a quaternion :

$$\left. \begin{aligned} \Delta(it+ju+kv) &= -\left(\frac{dt}{dx} + \frac{du}{dy} + \frac{dv}{dz}\right) \\ &+ i\left(\frac{dv}{dy} - \frac{du}{dz}\right) + j\left(\frac{dt}{dz} - \frac{dv}{dx}\right) + k\left(\frac{du}{dx} - \frac{dt}{dy}\right) \end{aligned} \right\} . . . \quad (\text{e.})$$

In fact the equations (a.) give generally (see art. 21 of the present series),

$$\left. \begin{aligned} (ix+jy+kz)(it+ju+kv) &= -(xt+yu+zv) \\ &+ i(yv-zu) + j(zt-xv) + k(xu-yt), \end{aligned} \right\} . . . \quad (\text{f.})$$

if  $xyztuv$  denote any six real numbers ; and the calculations by which this is proved, show, still more generally, that the same transformation must hold good, if each of the three symbols  $i, j, k$ , subject still to the equations (a.), be commutative in arrangement, as a symbolic factor, with each of the three other symbols  $x, y, z$ ; even though the latter symbols, like the former, should not be commutative in that way among themselves ; and even if they should denote symbolical instead of numerical multipliers, possessing still the distributive character. We may therefore change the three symbols  $x, y, z$ , respectively, to the three characteristics of partial differentiation,  $\frac{d}{dx}, \frac{d}{dy}, \frac{d}{dz}$ ; and thus the formula (e.) is seen to be included in the formula (f.). And if we then, in like manner, change the three symbols  $t, u, v$ , regarded as factors, to  $\frac{d}{dx'}, \frac{d}{dy'}, \frac{d}{dz'}$ , that is, to the characteristics of three partial differentiations performed with respect to three new and independent variables  $x', y', z'$ , we shall thereby change  $\frac{dt}{dx}$  to  $\frac{d}{dx} \frac{d}{dx'}$ , and so obtain the formula :

$$\left. \begin{aligned} \left(i\frac{d}{dx} + j\frac{d}{dy} + k\frac{d}{dz}\right)\left(i\frac{d}{dx'} + j\frac{d}{dy'} + k\frac{d}{dz'}\right) \\ = -\left(\frac{d}{dx}\frac{d}{dx'} + \frac{d}{dy}\frac{d}{dy'} + \frac{d}{dz}\frac{d}{dz'}\right) \\ + i\left(\frac{d}{dy}\frac{d}{dz'} - \frac{d}{dz}\frac{d}{dy'}\right) + j\left(\frac{d}{dz}\frac{d}{dx'} - \frac{d}{dx}\frac{d}{dz'}\right) \\ + k\left(\frac{d}{dx}\frac{d}{dy'} - \frac{d}{dy}\frac{d}{dx'}\right); \end{aligned} \right\} . . . \quad (\text{g.})$$

*On the Equation in Numbers Ax<sup>3</sup> + By<sup>3</sup> + Cz<sup>3</sup> = Dxyz.* 293  
which includes the formula (c.), and is now for the first time published.

This formula (g.) is, however, seen to be a very easy and immediate consequence from the author's fundamental equations of 1843, or from the relations (a.) of the foregoing article, which admit of being concisely summed up in the following continued equation:

$$i^2=j^2=k^2=ijk=-1. \dots \quad (h.)$$

The geometrical interpretation of the equation  $S_{\nu\tau\lambda\kappa}=0$  of the lines of curvature on the ellipsoid, with some other applications of quaternions to that important surface, must be reserved for future articles of the present series, of which some will probably appear in an early number of this Magazine.

[To be continued.]

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**XLVII. On the Equation in Numbers Ax<sup>3</sup> + By<sup>3</sup> + Cz<sup>3</sup> = Dxyz,  
and its associate system of Equations.** By J. J. SYLVESTER,  
Esq., M.A., F.R.S.\*

[Continued from p. 191.]

**I**N the last Number of this Magazine I gave an account of a remarkable transformation to which the equation

$$Ax^3 + By^3 + Cz^3 = Dxyz$$

is subject when certain conditions between the coefficients A, B, C, D are satisfied; which conditions I shall begin by expressing with more generality and precision than I was enabled to do in my former communication.

1. Two of the quantities A, B, C are to be to one another in the ratio of two cubes.

2.  $27ABC - D^3$  must contain no positive prime factor whatever of the form  $6n+1$ . I erred in my former communication in not excluding cubic factors of this form.

3. If  $2^m$  is the highest power of 2 which enters into ABC, and  $2^n$  the highest power of 2 which enters into D, then either  $m$  must be of the form  $3n \pm 1$ , or if not, then  $m$  must be greater than  $3n$ .

These three conditions being satisfied, the given equation can always be transformed into another,

where  $A'u^3 + B'v^3 + C'w^3 = D'uvw$ ,

$A'B'C' = ABC$   $D' = D$   $uvw = a$  factor of  $z$ .

The consequence of this is, as stated in my former paper, that wherever A, B, C, D, besides satisfying the conditions above stated, are taken so as likewise to satisfy the condition,—  
1°, of ABC being equal to  $2^{3m \pm 1}$ , or 2°, of ABC being equal to  $2^{3m \pm 1} \cdot p^{3n \pm 1}$ , provided in the first case that ABC is also of the

\* Communicated by the Author.

form  $9n \pm 1$ , and in the second case ABC again of the same form  $9m \pm 1$ , but likewise D divisible by 9, p being in both cases a prime, then the given equation will be *generally* insoluble. And I am now enabled to add that the *only* solution of which it will in any case admit, is the solitary one found by making two of the terms  $Ax^3$ ,  $By^3$ ,  $Cz^3$  equal to one another; so that, for instance, if the given equation should be of the form

$$x^3 + y^3 + ABC \cdot z^3 = Dxyz,$$

then the above conditions being satisfied, the one solitary solution of which the equation can possibly admit, is  $x=1$   $y=1$ ,

$$Az^3 - Dz + 2 = 0,$$

which may or may not have possible roots. I call this a *solitary* or singular solution, because it exists alone and no other solution can be deduced from it; whereas in general I shall show that any one solution of the equation

$$Ax^3 + By^3 + Cz^3 = Dxyz$$

can be made to furnish an infinity of other solutions independent of the one supposed given, *i. e.* not reducible thereto by expelling a common factor from the new system of values of  $x, y, z$  deduced from the given system.

The following is the Theorem of Derivation in question:

Let

$$A\alpha^3 + B\beta^3 + C\gamma^3 = D\alpha\beta\gamma.$$

Then if we write

$$F = A\alpha^3 \quad G = B\beta^3 \quad H = C\gamma^3,$$

and make

$$x = F^2G + G^2H + H^2F - 3FGH$$

$$y = FG^2 + GH^2 + HF^2 - 3FGH$$

$$z = \frac{1}{D} \{ F^3 + G^3 + H^3 - 3FGH \},$$

or

$$= \alpha\beta\gamma \{ F^2 + G^2 + H^2 - FG - FH - GH \},$$

we shall have

$$x^3 + y^3 + ABCz^3 = Dxyz.$$

I am hence enabled to show that whenever  $x^3 + y^3 + Az^3 = Dxyz$  is insoluble, there will be a whole family of allied equations equally insoluble. For instance, because  $x^3 + y^3 + z^3 = 0$  is insoluble in integer numbers. I know likewise that

$$x^6 + y^6 + z^6 = x^3y^3 + x^3z^3 + y^3z^3$$

$$x^6 + y^6 + z^6 = x^3y^3 + x^3z^3 - 2y^3z^3$$

are each equally insoluble.

In fact

$$\begin{aligned} & (x^3 + y^3 + z^3) \times (x^6 + y^6 + z^6 - x^3y^3 - x^3z^3 - y^3z^3) \\ & \times (x^6 + y^6 + z^6 - x^3y^3 - x^3z^3 + 2y^3z^3) \\ & \times (x^6 + y^6 + z^6 - y^3z^3 - y^3x^3 + 2x^3z^3) \\ & \times (x^6 + y^6 + z^6 - x^3z^3 - z^3y^3 + 2y^3x^3) \\ & = u^3 + v^3 + w^3, \end{aligned}$$

where  $u, v, w$  are rational integral functions of  $x, y, z$ .

Hence each of the factors must be incapable of becoming zero\*.

As a particular instance of my general theory of transformation and elevation, take the equation

$$x^3 + y^3 + 2z^3 = Mxyz.$$

Then, with the exception of the singular or solitary solution  $x=1, y=1$ , of which I take no account, I am able to affirm that for all values of  $M$  between 7 and  $-6$ , both inclusive, with the exception of  $M=-2$ , the equation is insoluble in integer numbers.

Take now the equation where  $M=-2$ , viz.

$$x^3 + y^3 + 2z^3 + 2xyz = 0.$$

One particular solution of this is

$$x=1 \quad y=-1 \quad z=1.$$

Another, which I shall call the second †, is

$$x=1 \quad y=3 \quad z=-2.$$

From the first solution I can deduce in succession the following:

$$\begin{array}{lll} x=11 & y=5 & z=-7 \\ x=-793269121 & y=117949000 & z=-1189735855 \\ & \text{&c.} & \text{&c.} \end{array}$$

From the second,

$$\begin{array}{lll} x=-10085 & y=8921 & z=-8442 \\ x=\text{&c.} & y=\text{&c.} & z=\text{&c.} \end{array}$$

As another example, take the equation

$$x^3 + y^3 + 6z^3 = 6xyz.$$

One solution of the transformed equation

$$u^3 + 2v^3 + 3w^3 = 6uvw$$

is evidently

$$u=1 \quad v=1 \quad w=1.$$

\* It is however sufficiently evident from their intrinsic form, which may be reduced to  $\frac{1}{4}(M^2 + 3N^2)$ , that this impossibility exists for all the factors except the first.

† See Postscript.

Hence I can deduce an infinite series of solutions of the given equation, of which the first in order of ascent will be

$$x=5 \quad y=7 \quad z=3.$$

Again, the lowest possible solution in integers of the equation

$$x^3+y^3+6z^3=0$$

will be

$$x=17 \quad y=37 \quad z=-21.$$

The equation

$$x^3+y^3+9z^3=0$$

admits of the solutions

$$x=1 \quad y=2 \quad z=-1$$

$$x=-271 \quad y=919 \quad z=-438.$$

I trust that my readers will do me the justice to believe that I am in possession of a strict demonstration of all that has been here advanced without proof. Certain of the writer's friends on the continent have, in their comments upon one of his former papers which appeared in this Magazine, complimented his powers of divination at the expense of his judgement, in rather gratuitously assuming that the author of the Theory of Elimination was unprovided with the demonstrations, which he was too inert or too beset with worldly cares and distractions to present to the public in a sufficiently digested form. The proof of whatever has been here advanced exists not merely as a conception of the author's mind, but fairly drawn out in writing, and in a form fit for publication.

P.S. It must not be supposed that the two primary or basic solutions above given of the equation

$$x^3+y^3+2z^3+2xyz=0,$$

viz.

$$x=1 \quad y=-1 \quad z=1$$

$$x=1 \quad y=3 \quad z=-2$$

are independent of one another. The second may be derived from the first, as I shall show in a future communication. In fact there exist *three* independent processes, by combining which together, one particular solution may be made to give rise to an infinite series of infinite series of infinite series of correlated solutions, which it may possibly be discovered contain between them the *general* complete solution of the equation

$$x^3+y^3+Az^3=Dxyz.$$

J. J. S.

26 Lincoln's Inn Fields,

Sept. 20, 1847.

[To be continued.]

**XLVIII. On the Invention and First Introduction of Mr. Koenig's Printing Machine. By RICHARD TAYLOR, F.S.A.&c.**

"As a step in the progress of civilization the Steam Press can only be compared to the original discovery of Printing itself."—*Times Newspaper, July 29, 1847, on the death of Mr. J. Walter.*

MORE than a century after its introduction the first invention of the Art of Printing became a subject of long-continued controversy, remarkable for the insufficiency and fallacy of the most confident assertions resting upon pretended traditions and unsupported conjectures. And, as Hadrian Junius in 1575 first disputed the claims of Gutemberg after so long a period had elapsed, so did Atkyns as late as 1664 first deny the title of Caxton to the honour of having introduced the art into our own country. Hence one of the writers in this controversy remarks that "the Art of Printing, which has given light to most other things, hides its own head in darkness."

It will be our own fault if we allow any unfounded assertions and pretensions to obtain currency with regard to an improvement in the art, of which *The Times* newspaper has said that "from the days of Faust and Gutemberg to the present hour there has been only one great revolution in the art of printing, and it occurred in the year 1814. Of that revolution Mr. Walter was the prominent and leading agent."

Now though I would on no account detract from the general merits of the late Mr. Walter, as set forth in the Obituary and extended Memoir which appeared in *The Times* of the 29th of July and 16th of September, yet I cannot allow the representations which are made in these articles, as to any share which he is alleged to have had in this important invention, to pass without the most unqualified contradiction.

In the Obituary we read as follows :—

"But one achievement alone is sufficient to place Mr. Walter high in that list which the world, as it grows older and wiser, will more and more appreciate—

‘Inventas aut qui vitam excoluere per artes,  
Quique sui memores alios fecere merendo.’

He first brought the steam-engine to the assistance of the public press. Familiar as the discovery is now, there was a time when it seemed fraught with difficulties as great as those which Fulton has overcome on one element and Stephenson on another. To take off 5000 impressions in an hour was once as ridiculous a conception as to paddle a ship fifteen miles against wind and tide, or to drag in that time a train of carriages weighing 100 tons fifty miles. Mr. Walter, who, without being a visionary, may be said to have thought nothing impossible that was useful and good, was early resolved that there should be no impossibility in printing by steam. It took a long time in those days to strike off the 3000 or 4000 copies of *The*

**Times.** Mr. Walter could not brook the tedium of the manual process. As early as the year 1804 an ingenious compositor, named Thomas Martyn, had invented a self-acting machine for working the press, and had produced a model which satisfied Mr. Walter of the feasibility of the scheme. Being assisted by Mr. Walter with the necessary funds, he made considerable progress towards the completion of his work."

"On the very eve of success he was doomed to bitter disappointment. He had exhausted his own funds in the attempt, and his father, who had hitherto assisted him, became disheartened, and refused him any further aid. The project was therefore for the time abandoned." [Why abandoned, we may ask, if so feasible, and on the very eve of success?]

"Mr. Walter, however, was not the man to be deterred from what he had once resolved to do. He gave his mind incessantly to the subject, and courted aid from all quarters, with his usual munificence. In the year 1814 he was induced by a clerical friend, in whose judgement he confided, to make a fresh experiment; and accordingly the machinery of the amiable and ingenious Koenig, assisted by his young friend Bauer, was introduced—not, indeed, at first, into *The Times* office, but into the adjoining premises, such caution being thought necessary from the threatened violence of the pressmen. Here the work advanced, under the frequent inspection and advice of the friend alluded to. At one period these two able mechanics suspended their anxious toil, and left the premises in disgust. After the lapse, however, of about three days, the same gentleman discovered their retreat\*, induced them to return, showed them to their surprise their difficulty conquered, and the work still in progress."

Who would not infer from the above, that Mr. Walter, having determined "to make a fresh experiment," in pursuance of those which he had long before abandoned (notwithstanding his early resolution that there should be no impossibility in it), and "courting aid from all quarters with his usual munificence," had been actually the person that enabled Mr. Koenig to pursue his labours on Mr. Walter's premises, "under the inspection and advice of Mr. Walter's clerical friend," and thus to produce his invention? Whereas, in truth, Mr. Walter knew nothing of Mr. Koenig till after his invention had been completed. He was merely the first newspaper proprietor who purchased from the Patentees the Printing Machines long before invented by Mr. Koenig. Of these patentees I was one, and as I am now the sole survivor, it devolves upon me to contradict any erroneous statements and unfounded pretensions. I feel this to be the more necessary, as already the misstatements of *The Times* are circulated, with additions and exaggerations, in other journals.

\* To me this story appears not a little extraordinary:—the "discovery of the retreat" of Messrs. K. and B.! who were every day to be found superintending our factory in Whitecross Street.—R. T.

Thus, in an article in the Mechanics' Magazine for Sept. 18, copied into the newspapers, I find the following passage :—

" No sooner were presses made of iron, than the idea occurred of working them by steam ; and the first to welcome the new and happy thought was the proprietor of a journal which stood in instant need of some such powerful auxiliary to enable him to keep pace with a circulation unexampled in the history of the press, and who, without it, would most assuredly never have been able to attain to that prodigious influence which for many years past has at once astonished and awed the world. Koenig, the ingenious inventor of the steam-press\*, found in the proprietor of The Times his natural and best possible patron. *With the liberal aid of the late Mr. Walter, he produced a machine of somewhat gigantic size, but nevertheless possessing a completeness of design and purpose which cast all other surface printing-presses into the shade.*"

And again—

" The steam-press has given occupation to many thousands, who, but for its introduction, would have been standing idle, and who ought, one and all, to bless the memory of Mr. Walter for enabling the inventor to work out his ideas, and perfect his great and glorious undertaking."

Now the whole of this is a fable. Mr. Walter was no "natural and best possible patron" of Mr. Koenig's,—gave him no "liberal aid in producing his machine," nor did anything whatever to "enable him to work out his ideas." These had all been worked out long before; patents had been taken out, a machine had been made, and was in operation on the premises of the Patentees, before ever Mr. Walter, or any other newspaper proprietor, was applied to and invited to adopt it. Mr. Perry of the Morning Chronicle declined, alleging that he did not consider a newspaper worth so many years' purchase as would equal the cost of machines. Mr. Walter, "being a cautious man of the world," but enterprizing, "it being," as his biographer says, "his habit in the game of life never to throw away a chance," when he had fully satisfied himself by seeing that the invention was accomplished, and in effective operation, consented to give an order for two machines, for the cost of which he paid us a certain sum, and a rental according to the number of copies printed; and this rent we received, until it was commuted for a sum agreed upon.

I do not mean to charge the writer in the Mechanics' Magazine with any intentional misrepresentation. He has evidently been misled by the articles in The Times, which though they do not *directly* assert all that he has inferred from them, yet they imply as much. Thus a story gains in the telling,

\* Mr. Koenig's invention is very inappropriately designated by the terms "steam-press," and "the working of iron presses by steam." Its construction is wholly independent of the motive power employed.

till the most vague and unfounded suggestions, if uncontradicted, are assumed as indisputable facts; and it would be recorded that if Koenig was the Gutenberg of the new discovery, Walter was at least the Faust or Schœffer of the affair, or rather, both in one.

I am convinced that Mr. Walter, were he living, would disclaim the pretensions that have been made in his name: and indeed he has done so in the announcement which appeared in *The Times*, Nov. 20, 1814, the day on which that journal was first printed by the machines, and which contains the following passage:—

“That the completion of an invention of this kind, not the effect of chance, but the result of mechanical combinations methodically arranged in the mind of the artist, should be attended with many obstructions and much delay may be readily admitted. Our share in the event has indeed only been the application of the discovery, under an agreement with the patentees, to our own particular business.”

“The time for effecting the great revolution in the art of printing,” says Mr. Walter’s biographer, “did not arrive till the year 1814.” Now it was in 1809 that, together with the late Mr. George Woodfall, I joined Mr. Koenig and Mr. Bensley in taking out patents\*, the machine being even then so far advanced as to satisfy us as to the prospect of success, and to enable us to have the specifications drawn up. Koenig had gone on with Bensley, to whom I had recommended him some few years before, up to the year 1809, when the taking of premises and the purchase of lathes, tools, &c., and the employing of workmen, with the salaries of Mr. Koenig and his able and excellent assistant Mr. Bauer, led Bensley to invite us to a partnership in the undertaking. For several years it occupied much of our time and attention, and cost us much money (from which we had no return †) and much anxiety. Each experiment suggested some improvement, and one improvement led to others, so that additional patents had to be taken out. But with Mr. Walter we had none of us any communication, until, as I have before stated, the machine had been completed and was at work on our own premises.

I have thought it right, under the circumstances, to put on

\* One of the four patents bears date March 29, 1810 (See *Phil. Mag.* vol. xxxv. 1st Series, p. 319). It was taken out in the name of Frederick Koenig, and was assigned by articles of partnership to the firm of Bensley, Koenig, Woodfall and Taylor.

† Mr. Koenig left England, suddenly, in disgust at the treacherous conduct of Bensley, always shabby and overreaching, and whom he found to be laying a scheme for defrauding his partners in the patents of all the advantages to arise from them. Bensley, however, while he destroyed the prospects of his partners, outwitted himself, and grasping at all, lost all, becoming bankrupt in fortune as well as in character.

record my own recollections as to the progress and introduction of this invention : and though they relate to transactions which took place from thirty to forty years ago, I believe they are in the main correct, and can be confirmed by documentary evidence.

## XLIX. *Proceedings of Learned Societies.*

### CAMBRIDGE PHILOSOPHICAL SOCIETY.

[Continued from p. 143.]

**O**N the Partitions of Numbers, on Combinations, and on Permutations. By Henry Warburton, M.P., F.R.S., F.G.S., Member of the Senate of the University of London ; formerly of Trinity College, A.M.

The use made by Waring of the Partitions of numbers in developing the power of a polynome, induced the author to seek for some general and ready method of determining in how many different ways a given number can be resolved into a given number of parts. On his communicating the method described in article 5 of Section I. of this abstract, to Professor De Morgan, in the autumn of 1846, that gentleman intimated a wish that the author would turn his attention also to Combinations ; and such was the origin of the researches which form the subject of the 2nd and 3rd sections.

#### I. *On the Partitions of Numbers.*

1. Let  $[N, p_n]$  denote how many different ways there are of resolving the integer  $N$  into  $p$  integral parts, none less than  $\eta$ . Then

$$[N, p_n] = [N \pm p\theta, p_{n \pm \theta}]. \quad \dots \quad (I.)$$

2. Such of the  $p$ -partitions of  $N$  as contain  $\eta$  as a part, and no part less than  $\eta$ , are obtained by resolving  $N - \eta$  into  $p - 1$  parts not less than  $\eta$ , and by adding  $\eta$ , as a  $p$ th part, to every such  $(p - 1)$ -partition. That is,

$$[N, p_n] - [N, p_{n+1}] = [N - \eta, p - 1]. \quad \dots \quad (II.)$$

3. In (II.), substitute  $\eta + 1, \eta + 2, \&c.$  successively for  $\eta$ . The sum of the results is

$$[N, p_n] - [N, p_{n+\theta+1}] = S_0^{\theta} [N - \eta - zp, p - 1]. \quad \dots \quad (III.)$$

In this expression, when  $\theta = I^*(\frac{N}{p}) - \eta$ , the term  $[N, p_{n+\theta+1}]$  vanishes, and the formula then becomes analogous to one published anonymously by Professor De Morgan in a paper printed in the fourth volume, p. 87, of the Cambridge Mathematical Journal.

4. In (II.), for  $[N, p_{n+1}]$  substitute  $[N - p\eta, p_1]$ , and transpose

\*  $I\left(\frac{N}{p}\right)$  is employed to avoid the long phrase, "the integer nearest to and not exceeding  $\frac{N}{p}$ ."

the terms. Then

$$[N, p_\eta] - [N - \eta, p_{\eta-1}] = [N - p\eta, p_1]; \dots \quad (\text{IV.})$$

and this leads to

$$[N - \eta, p_{\eta-1}] - [N - 2\eta, p_{\eta-2}] = [N - p\eta, p_{\eta-1}];$$

and that leads to the summation

$$[N, p_\eta] = S_0^p [N - p\eta, z_1]. \dots \quad (\text{V.})$$

The lower limit of  $z$  in (V.) is made 0, in order that the formula may comprehend the extreme case  $[0, 0_1] = 1$ , analogous to the extreme case in Combinations.

5. After substituting 1 for  $\eta$ , the author applies formula (IV.) to determining in how many different ways  $N$  can be resolved into  $p$  parts not less than 1. Let  $[N, p_1]$  be the term in a table of double entry corresponding to column  $N$ , line  $p$ , in the table. From the head, in line 0, of each of the columns 0, 1, 2, 3, &c., draw a diagonal, advancing one column and one line at a time. Take these diagonals one after another, and in each of them compute by formula (IV.) the terms situate on lines 0, 1, 2, 3, &c., one by one in succession. If  $N$  be the number at the head of the column from which any diagonal takes its departure, there will be only  $N$  terms to compute on that diagonal, the further terms being only repetitions of the term on the line  $N$ . For the diagonal in question intersects line  $N$  in column  $2N$ ; and, by formula V,

$$[2N, N_1] = S_0^N [N, z_1]$$

= the sum of all the terms in column  $N$ . But, moreover,

$$[2N + y, N_1 + y] = S_0^N [N, z_1]$$

= the same constant. The leading property of the table, indicated by the formula

$$[N, p_1] = S_0^p [N - p, z_1],$$

is, that the term  $[N, p_1] =$  the sum of all the terms in column  $N - p$ , from line 0 to line  $p$  inclusive. After the publication of the anonymous paper before referred to, Professor De Morgan discovered this theorem also, but he did not announce it\*.

## II. On Combinations.

1. In ordinary Combinations, the combining elements are of different kinds, and there is but one element of a kind : in the case here considered, there are different kinds of elements, and there may be many elements of a kind ; and more than one element of a kind may enter into the same combination.

2. If  $u$  elements enter at a time into each combination, and the

\* The author has recently discovered an equivalent formula in p. 264 of Euler's Int. in An. Infinitorum; but investigated by a totally different method, and not applied as the author has applied it.

kinds are determinate in number, and their number is  $s$ , let  $\left\{ \begin{matrix} u \\ s \end{matrix} \right\}$  denote how many different combinations can then be formed: if the elements are determinate in number, and their number is  $\sigma$ , let the number of the combinations which can then be constructed, be denoted by  $\{u, \sigma\}$ . If  $\varphi(x)$  be any function of  $x$ , let  $D^u \varphi(x)$  denote the coefficient of  $x^u$  in that function developed according to the powers of  $x$ .

3. The same things as before being assumed, let a given set of elements consist of  $\alpha$  elements of the kind A,  $+\beta$  elements of the kind B,  $+\&c.$ . Take the product, K, of the  $s$  geometrical progressions,

$$[1 + Ax + A^2x^2 + \dots + A^\alpha x^\alpha], [1 + Bx + B^2x^2 + \dots + B^\beta x^\beta], \&c.$$

Then K will be of the form,

$$1 + S[A]x + S[A^2 + AB]x^2 + S[A^3 + A^2B + ABC]x^3 + \&c.,$$

and  $D^u[K]$  will be of the form

$$S[A^\alpha B^\beta C^\gamma \&c.],$$

the last expression being an aggregate of terms of the form  $A^\alpha B^\beta C^\gamma \dots$ , each containing a different combination of  $u$  of the given elements, and their sum comprehending all the possible combinations of those elements taken  $u$  at a time. Now, if A, B, C, &c. be each made equal to 1, K will become

$$k = [1 + x + x^2 + \dots + x^\alpha][1 + x + x^2 + \dots + x^\beta]. \&c.;$$

each of the terms  $A^\alpha B^\beta C^\gamma \&c.$  will become 1, and the number of all the terms of the form  $A^\alpha B^\beta C^\gamma \dots$  which  $D^u[K]$  or  $S[A^\alpha B^\beta C^\gamma \dots]$  contains, that is to say,  $\{u, \sigma\}$  will be represented by  $D^u[k]$ ; which latter coefficient the author next proceeds to determine.

Now

$$k = \frac{1-x^{\alpha+1}}{1-x} \cdot \frac{1-x^{\beta+1}}{1-x} \cdot \&c. = [1-x^{\alpha+1}][1-x^{\beta+1}] \dots [1-x]^{-s} \\ = [1-x^{\alpha+1}][1-x^{\beta+1}] \dots S_0^\infty \left[ \frac{s^{u-1}}{1-u} x^u \right] \quad \left. \right\} (VI.)$$

$$= [1-x^{\alpha+1}][1-x^{\beta+1}] \dots \frac{1}{1^{s-1}|1|} S_0^\infty \left[ [u+1]^{s-1} |1| x^u \right] (VII.)$$

For brevity, write  $u_1, \alpha_1, \beta_1, \&c.$  respectively, for  $u+1, \alpha+1, \beta+1, \&c.$ ; and also write [1] for  $[1-x]^{-s}$ ; [2] for  $[1-x^{\alpha_1}][1-x]^{-s}$ ; that is, for  $[1-x^{\alpha_1}] \cdot [1]$ ; [3] for  $[1-x^{\alpha_1}][1-x^{\beta_1}][1-x]^{-s}$ ; that is, for  $[1-x^{\beta_1}] \cdot [2]$ , and so on. Then

$$D^u[2] = D^u[1] - D^{u-\alpha_1}[1];$$

and

$$D^u[3] = D^u[2] - D^{u-\beta_1}[2];$$

\* According to the factorial notation, here used by the author,  $s^{u-1}$  represents  $s[s-1][s-2]\dots[s-(u-1)]$ .

and

$$D^u[4] = D^u[3] - D^{u-\alpha_1}[3]; \text{ and so on; (VIII.)}$$

and the developed product of the binomes,

$$[1-x^{\alpha_1}][1-x^{\beta_1}][1-x^{\gamma_1}], \text{ &c.};$$

that is to say,

$$\begin{aligned} 1-x^{\alpha_1}+x^{\alpha_1+\beta_1}-x^{\alpha_1+\beta_1+\gamma_1}+ & \text{ &c.} \\ -x^{\beta_1}+x^{\alpha_1+\gamma_1}- & \text{ &c.} \\ -x^{\gamma_1}+x^{\beta_1+\gamma_1} & \\ -\text{ &c.} + \text{ &c.} & \end{aligned}$$

when multiplied into the development of  $[1-x]^{-s}$ ,

manifestly leads to the following formula :

$$D^u[m] = D^u[1] - S \left[ D^{u-\alpha_1}[1] \right] + S \left[ D^{u-\alpha_1-\beta_1}[1] \right] - S \left[ D^{u-\alpha_1-\beta_1-\gamma_1}[1] \right] + \text{ &c.} \quad \text{(VIII*.)}$$

where, since the powers of  $x$ , in (VI.) or (VII.) developed, are to be all positive, no expression of the form

$$(u-\alpha_1), (u-\alpha_1-\beta_1), (u-\alpha_1-\beta_1-\gamma_1), \text{ &c.}$$

is to be negative. Then by giving to

$$D^u[1], D^{u-\alpha_1}[1], D^{u-\alpha_1-\beta_1}[1], \text{ &c. . . (IX.)}$$

their respective values, we obtain the series of expressions :

$$D^u[1] = \frac{1}{1^{s-1|1}} u_1^{s-1|1} = \frac{s^{u|1}}{1^{u|1}} = \left[ \begin{matrix} u \\ s \end{matrix} \right]$$

where in all the kinds the elements are plural without limit ; a formula given by Hirsch :

$$D^u[2] = \frac{1}{1^{s-1|1}} \left[ u_1^{s-1|1} - [u_1 - \alpha_1]^{s-1|1} \right] = \left[ \begin{matrix} u \\ s \end{matrix} \right]$$

where the elements A are limited in number to  $\alpha$ , but those of the other  $(s-1)$  kinds are plural without limit :

$$D^u[3] = \frac{1}{1^{s-1|1}} \left[ u_1^{s-1|1} - [u_1 - \alpha_1]^{s-1|1} + [u_1 - \alpha_1 - \beta_1]^{s-1|1} - [u_1 - \beta_1]^{s-1|1} \right] = \left[ \begin{matrix} u \\ s \end{matrix} \right]$$

where, moreover, the elements B are limited in number to  $\beta$ , but those of the other  $(s-2)$  kinds are plural without limit : and so for the rest. The law of the terms being evident, they need not be continued further.

Example of (IX.). Given one element of 1 kind, two elements of a 2nd kind, three of a 3rd, and four of a 4th ; and let  $u=5$ . Then

$$\{u, \sigma\} = \frac{1}{1.2.3} \left( \begin{matrix} -4.5.6 \\ 6.7.8 \\ -3.4.5 + 1.2.3 \\ -2.3.4 \\ -1.2.3 \end{matrix} \right) = 22.$$

4. If  $\alpha=\beta=\gamma=\&c.$ , formula (IX.) becomes

$$\{u, \sigma\} = \frac{1}{1^{s-1|1}} \sum_{\theta=0}^s \binom{u_1}{\alpha_1} \left[ (-1)^{\theta} \frac{s^{\theta}-1}{1^{\theta|1}} [u_1 - \theta \alpha_1]^{s-1|1} \right]. \quad (\text{X.})$$

Example of formula (X.) Given seven kinds of elements, and three of each kind; and let  $u=4$ . Then

$$\{u, \sigma\} = \frac{1}{1.2.3.4.5.6} [5.6.7.8.9.10 - 7.1.2.3.4.5.6] = 203.$$

5. If it is required to determine many, or all, of the terms of the series  $\{0, \sigma\}, \{1, \sigma\}, \{2, \sigma\}, \dots, \{\sigma, \sigma\}$ , formulas (VIII.) suggest the following process for the determination of those terms. An example will best explain the process.

Given 1 element of one kind, 2 elements of a second kind, and 3 of a third kind. How many combinations can be formed from these elements, when taken 0, 1, 2, 3, 4, 5, 6 at a time, respectively?

Values of $u$ .....	0	1	2	3	4	5	6
Coefficients of $x^u$ in $[1-x]^{-3}$ .....	1	3	6	10	15	21	28
Multiply by $[1-x^2]$ ; that is, subtract .....	...	...	1	3	6	10	15
Coefficients of $x^u$ in $[1-x^2][1-x]^{-3}$ .....	1	3	5	7	9	11	13
Multiply by $[1-x^3]$ ; that is, subtract .....	...	...	...	1	3	5	7
Coefficients of $x^u$ in $[1-x^2][1-x^3][1-x]^{-3}$ .....	1	3	5	6	6	6	6
Multiply by $[1-x^4]$ ; that is, subtract .....	...	...	...	...	1	3	5
Coefficients of $x^u$ in $[1-x^2][1-x^3][1-x^4] \{[1-x]^{-3}\}$ .....	1	3	5	6	5	3	1
That is .....	$\{0, \sigma\}$	$\{1, \sigma\}$	$\{2, \sigma\}$	$\{3, \sigma\}$	$\{4, \sigma\}$	$\{5, \sigma\}$	$\{6, \sigma\}$

6. Let a set of elements, S, such as we have been previously considering, consist of two similar sets, T and T', which do not contain in common any elements of the same kind. If S consists of  $\sigma$  elements combining  $u$  at a time, and T consists of  $\tau$  elements combining  $v$  at a time, T' will consist of  $(\sigma-\tau)$  elements combining  $(u-v)$  at a time. Consider  $u$  as constant, for the moment, and  $v$  as variable. The author then shows that if by the process described in art. 5, the whole series of terms  $\{v, \tau\}$  and the whole series of terms  $\{u-v, \sigma-\tau\}$ , have been determined, we can thence determine the whole series of terms  $\{u, \sigma\}$  by means of the formula

$$\{u, \sigma\} = \sum_v \binom{\tau}{v} [\{v, \tau\} \cdot \{u-v, \sigma-\tau\}] ; \quad . \quad . \quad . \quad (\text{XI.})$$

and of this he gives examples.

7. In formula (XI.) substitute  $(\sigma-u)$  for  $u$ ; and develop  $\{u, \sigma\}$  and  $\{\sigma-u, \sigma\}$  in the manner indicated by that formula. By comparing the 1st, 2nd, 3rd, &c. terms respectively of  $\{u, \sigma\}$  with the last, last but one, last but two, &c. terms of  $\{\sigma-u, \sigma\}$ , and vice

versd, the author shows that  $\{u, \sigma\}$  will be identical with  $\{\sigma-u, \sigma\}$ , provided  $\{v, \tau\}$  is identical with  $\{\tau-v, \tau\}$ , and provided also  $\{u-v, \sigma-\tau\}$  is identical with  $\{\sigma-\tau-(u-v), \sigma-\tau\}$ . But this identity actually exists when T consists of elements of one kind only, and when T' also consists of elements of one kind only. For, in that case, every term of the series  $\{v, \tau\}$  and every term of the series  $\{u-v, \sigma-\tau\}$  is equal to 1. Let the elements of the single kind which T contains, be different from those of the single kind which T' contains. Then the identity in question will exist, when S consists of elements, finite in number, of two different kinds: consequently, it exists also when T consists of elements, finite in number, of two different kinds, and T' consists of elements, finite in number, of one or two other kind or kinds; that is, when S consists of elements, finite in number, of three or four different kinds. And therefore universally, in the case as well of finitely plural, as of singular elements, the following law obtains:

$$\{u, \sigma\} = \{\sigma-u, \sigma\}. . . . . \quad (\text{XII.})$$

Hence it follows that in applying formulas (IX.) and (X.) to particular cases, the labour of computation will be shortened by substituting for the variable the lesser of the two numbers  $u$  and  $\sigma-u$ .

8. The author next considers how many different combinations can be formed from a given set of elements, when every combination is to be constructed in conformity with a given type; in which type there are  $m$  different kinds containing  $v$  elements each,  $m'$  other different kinds containing  $v'$  elements each,  $m''$  other different kinds containing  $v''$  elements each, and so on; and where, consequently, in each combination,  $z$ , the number of kinds, is  $m+m'+m''+ \&c.$ ; and  $u$ , the number of elements, is  $mv+m'v'+m''v''+ \&c.$  The type remaining constant, any combination conformable thereto may be altered, either by changing the particular  $z$  kinds which are selected out of the  $s$  given kinds; or, the kinds remaining the same, by altering the distribution of the parts  $v, v, v, \dots (m)v', v', v', \dots (m')v'', v'', v'', \dots (m'')$  &c., among those kinds. When all the elements are plural without limit, the changes of the former description will be represented by

$$\frac{s^{z|-1}}{1^{z|1}};$$

and those of the latter description by

$$\frac{1^{z|1}}{1^{m|1}. 1^{m'|1}. 1^{m''|1} \dots},$$

and their joint effect by the product

$$\frac{s^{z|-1}}{1^{z|1}} \times \frac{1^{z|1}}{1^{m|1}. 1^{m'|1}. 1^{m''|1} \dots} \cdot \cdot \cdot \quad (\text{XIII.})$$

But when the elements of all the given kinds are finite in number, class these kinds, so that each kind in class 1 contains not fewer

than  $v$  elements; each kind in class 2 contains fewer than  $v$ , but not fewer than  $v'$  elements; each kind in class 3 contains fewer than  $v'$ , but not fewer than  $v''$  elements; and so on; and so that the given kinds may in this way be reduced, say, to  $t$  kinds containing  $v$  elements each +  $T'$  kinds containing  $v'$  elements each +  $T''$  kinds containing  $v''$  elements each, &c. Then let  $t-m+T'=t'$ ;  $t'-m'+T''=t''$ ; and so on. The given kinds being thus ordered, since we are required to select, 1st,  $m$  out of  $t$  kinds; then, 2nd,  $m'$  out of  $t'$  kinds; then, 3rd,  $m''$  out of  $t''$  kinds; and so on; the number of the different combinations which can be constructed from those kinds in conformity with the type, will be

$$\frac{t^{m|-1}}{1^{m|1}} \cdot \frac{t'^{m'|-1}}{1^{m'|1}} \cdot \frac{t''^{m''|-1}}{1^{m''|1}}, \text{ &c. . . . . (XIV.)}$$

If  $tv+T'v'+T''v''\dots$  &c. is reduced to a single term,  $t.v$ ; then formula (XIV.) becomes

$$\frac{t^{z|-1}}{1^{m|1} \cdot 1^{m'|1} \cdot 1^{m''|1}}, \text{ &c. . . . . (XV.)}$$

Example of (XIV.). Given eight elements of 1 kind, seven of a 2nd kind, six of a 3rd, five of a 4th, four of a 5th, three of a 6th, two of a 7th, and one element of an 8th kind, out of which it is required to construct combinations, each consisting of three kinds with five elements each + two kinds with three elements each + one kind with two elements. Of such combinations there can be formed

$$\frac{4^{3|-1}}{1^{8|1}} \cdot \frac{3^{2|-1}}{1^{2|1}} \cdot \frac{2^{1|-1}}{1^{1|1}} = 24.$$

9. If it be required to determine how many different combinations can be constructed, each containing  $u$  elements of  $z$  kinds, and the given elements are all finite in number; we must form all the different  $z$ -partitions of  $u$ ; and each of these partitions being regarded as a type, we must determine, by formula (XIV.) or (XV.), how many combinations correspond to each of these types; and the total number required will be the sum of all these particular determinations. But if the given elements may all be repeated without limit, it follows from formula (XIII.), that the sum of all the particular determinations may be represented by

$$\frac{s^{z|-1}}{1^{z|1}} \times S \left( \frac{1^{z|1}}{1^{m|1} \cdot 1^{m'|1} \cdot 1^{m''|1}, \text{ &c.}} \right).$$

Now

$$S \left( \frac{1^{z|1}}{1^{m|1} \cdot 1^{m'|1} \cdot 1^{m''|1}} \right)$$

denotes how many different permutations can be formed, when, in each different  $z$ -partition of  $u$ , the parts are permuted  $z$  together at a time; and the number of such permutations is

$$\Sigma^{z-1}[1] = \Sigma^{z-2}[u-1] = \frac{[u-1]^{z-1|-1}}{1^{z-1|1}}.$$

Consequently the required sum is

$$\frac{s^{z|-1}}{1^{z|1}} \times \frac{[u-1]^{z-1|-1}}{1^{z-1|1}}. . . . . \quad (\text{XVI.})$$

If in (XVI.)  $z$  varies from 0 to  $u-1$ ,

$$\sum_{z=0}^{u-1} \left[ \frac{s^{z|-1}}{1^{z|1}} \times \frac{[u-1]^{z-1|1}}{1^{z-1|1}} \right] = \frac{s^{u|1}}{1^{u|1}},$$

this summation being a particular case of formula (XI.). The result agrees with  $D^u[1]$  formula (IX.), art. 3.

10. When the given elements are all finite in number, we may determine  $\{u, \sigma\}$ , by taking the sum of all the particular determinations that may be obtained pursuant to art. 9, by giving to  $z$  the successive values 0, 1, 2, 3, &c. If  $u < s$ , the upper limit of  $z$  is  $u$ , and the number of types to be formed is  $[2u, u_1]$ ; which becomes  $[2s, s_1]$ , if  $u=s$ . If  $u > s$ , the upper limit of  $z$  is  $s$ ; and the number of types to be formed is  $[u+s, s_1]$ . (See articles 4 and 5, Section I.) But, if the repetition is finite, some of these partitions may fail to yield combinations.

11. If the elements A, B, C, &c. represent different prime numbers, all the methods and theorems contained in this section will apply, *mutatis mutandis*, to the composite numbers of which those primes, or the powers of those primes, are divisors.

### III. On Permutations.

1. Let the given elements be of  $s$  different kinds. We can determine in two known cases, by an explicit function of  $u$ , when the elements are taken  $u$  at a time, in how many different ways they can be permuted. The number of the permutations is denoted, when there is but one element of a kind, by  $s^{u|-1}$ ; and when in all the kinds the elements are plural without limit, by  $s^u$ . When the plurality is finite, it is only in the particular case of all the elements being permuted at a time, that there is a known formula to express the number of their permutations.

2. Every combination constructed on a given type,  $u=mv+m'v'+m''v''+\&c.$ , will generate the same number of permutations,

$$\frac{1^{u|1}}{[1^{v|1}]^m [1^{v'|1}]^{m'} [1^{v''|1}]^{m''} \cdot \&c.} = P.$$

Therefore, if the number of the different combinations which can be constructed out of the given elements in conformity with that type, is represented by Q,  $Q \times P$  will be the number of the permutations corresponding to the type and to those elements. If the plurality be without limit,

$$\frac{s^{z|-1}}{1^{m|1} \cdot 1^{m'|1} \cdot 1^{m''|1} \cdot \&c.} \times P$$

will be the number of the permutations. If the given elements be finite in number, as in formulas (XIV.) and (XV.), the number of

the permutations corresponding to those elements and to the type, will be

$$\frac{t^{m|}-1}{1^{m|1}} \cdot \frac{t^{m'|}-1}{1^{m'|1}} \cdot \frac{t^{m''|}-1}{1^{m''|1}} \text{ &c. } \times P.$$

Every different partition of  $u$  that may be formed within the limits pointed out in art. 10, Section II., will give rise to a similar product,  $Q \times P$ ; and the sum of all these particular products,  $S[Q \times P]$ , will show how many different permutations can be formed from the given elements, taken  $u$  at a time. The author illustrates this method of computing the number of permutations, by examples.

3. Let  $P \left\{ \begin{matrix} u \\ s \end{matrix} \right\}$  denote how many different permutations can be formed when  $u$  elements are taken at a time out of  $s$  kinds; and  $P \{u, \sigma\}$  denote how many different permutations can be formed when  $u$  elements are taken at a time out of  $\sigma$ , a finite number of elements. If all the elements may be repeated without limit,

$$\begin{aligned} \left\{ \begin{matrix} u \\ s \end{matrix} \right\} &= D^u [1^{u|1} \cdot \varepsilon^{s|x}] = s^u \\ &= D^u \left[ 1^{u|1} \left[ 1 + x + \frac{x^2}{1.2} + \dots + \frac{x^u}{1^{u|1}} + \dots \right]^s \right]. \end{aligned}$$

Hence the author infers that, if the elements A are limited in number to  $\alpha$ , while those of the other  $(s-1)$  kinds are plural without limit,

$$P \left\{ \begin{matrix} u \\ s \end{matrix} \right\} = D^u \left[ 1^{u|1} \varepsilon^{(s-1)x} \left[ 1 + x + \frac{x^2}{1.2} + \dots + \frac{x^\alpha}{1^{\alpha|1}} \right] \right];$$

that if, moreover, the elements B are limited in number to  $\beta$ , while the other  $(s-2)$  kinds are plural without limit,

$$\begin{aligned} P \left\{ \begin{matrix} u \\ s \end{matrix} \right\} &= D^u \left[ 1^{u|1} \varepsilon^{(s-2)x} \left[ 1 + x + \frac{x^2}{1.2} + \dots + \frac{x^\alpha}{1^{\alpha|1}} \right] \right. \\ &\quad \left. \left[ 1 + x + \frac{x^2}{1.2} + \dots + \frac{x^\beta}{1^{\beta|1}} \right] \right]; \end{aligned}$$

and so on, until finally, if all the elements are finite in number, and the elements A, B, C, &c. are respectively limited, in point of number, to  $\alpha, \beta, \gamma, \&c.$ ,

$$P \{u, \sigma\} = D^u \left[ 1^{u|1} \left[ 1 + x + \dots + \frac{x^\alpha}{1^{\alpha|1}} \right] \left[ 1 + x + \dots + \frac{x^\beta}{1^{\beta|1}} \right] \right. \left. \left[ 1 + x + \dots + \frac{x^\gamma}{1^{\gamma|1}} \right] \right]. \quad (\text{XVII.})$$

4. Hence, if in all the  $s$  kinds the elements are dual, (XVII.) becomes

$$\left. \begin{aligned} P\{u, \sigma\} &= D_u \left[ 1^{u|1} \left[ 1 + x + \frac{x}{2} \right]^s \right] = \\ S_{\sigma}^I \left( \frac{u}{2} \right) &\left[ \frac{u^{2\sigma-1} \times s^{u-\sigma-1}}{2^{\sigma|2}} \right]. \end{aligned} \right\} \quad (\text{XVIII.})$$

This is the only addition which the author has been able to make to the cases wherein  $P\left[\frac{u}{s}\right]$ , or  $P\{u, \sigma\}$  is expressed by an explicit function of  $u$ , symmetrical in form.

Example. Let there be five kinds of elements, and two of each kind. Let  $u=3$ .

$$P\{u, \sigma\} = \frac{1.5.4.3}{1} + \frac{3.2 \times 5.4}{2} = 120.$$

5. The author gives the following theorem, which is precisely analogous to that of art. 6, Sect. II., formula (XI.), in Combinations; viz.

$$P\{u, \sigma\} = S_{\sigma|0}^{\tau} \left[ \frac{u^{\sigma|1}-1}{1^{\sigma|1}} P\{v, \tau\} \cdot P\{u-v, \sigma-\tau\} \right]. \quad (\text{XIX.})$$

6. By a mode of proof precisely analogous to that employed in art. 7, Sect. II., he shows that  $P\{\sigma-1, \sigma\} = P\{\sigma, \sigma\}$ ; that is to say, that

$$\frac{1^{\sigma|1}}{1^{\alpha|1}. 1^{\beta|1}. 1^{\gamma|1}. \&c.}$$

denotes the number of permutations that can be formed with  $\alpha$  elements A,  $\beta$  elements B, &c. (where  $[\alpha+\beta+\gamma+\&c.] = \sigma$ ), as well when  $\sigma=1$  elements, as when  $\sigma$  elements, are taken at a time.

Since correcting his paper for publication, the author has had his attention called to the work of Bézout on Elimination (4to. Paris, 1779, p. 469), as containing a formula similar in structure to that numbered VIII\*. in the present abstract.

Bézout investigates the composition of a polynome function of  $s$  quantities, A, B, C, &c., consisting of terms which are of the form  $A^\alpha B^\beta C^\gamma$ , and of every dimension from 0 to  $u$  inclusive. Let  $[s]^u$  denote such a polynome, complete in all its terms, and  $N[s]^u$  the number of its terms. Then, 1st,

$$N[s]^u = \frac{[u+1]^{s|1}}{1^{s|1}};$$

and 2nd, the number of the terms in  $[s]^u$  which are not divisible by either  $A^\alpha$ , or  $B^\beta$ , or  $C^\gamma$ , &c., he expresses by

$$\begin{aligned} N[s]^u - N[s]^{u-\alpha} + N[s]^{u-\alpha-\beta} - &\&c. \\ - N[s]^{u-\beta} + &\&c. \\ - &\&c. \end{aligned}$$

He also observes (p. 39) that when  $A^\alpha, B^\beta, C^\gamma, \&c.$  are the highest powers of A, B, C, &c. which a polynome, agreeing in other respects with  $[s]^u$ , contains, the terms of such incomplete polynome will agree in point of number with those terms in  $[s]^u$  which are not divisible by either  $A^{\alpha+1}$ , or  $B^{\beta+1}$ , or  $C^{\gamma+1}$ , &c. The polynomes from which Bézout proposes to eliminate certain terms, contain terms of all dimensions from 0 to  $u$  inclusive. The terms which are to remain after the others have been eliminated, and which are enumerated by means of the condition, that they are not divisible by certain powers of A, or B, or C, &c., may be of all dimensions indiscriminately from 0 to  $u$  inclusive. Bézout's object is exclusively Elimination, and he makes no allusion to any other application of his formulæ.

The polynomes considered by the author, taken in their entirety, agree in their general structure with those considered by Bézout; but the nature of the author's inquiries led him to confine his attention to the composition of those particular terms in a polynome which were of the same dimension; and to seek to express the number of the terms, not of all dimensions indiscriminately, but of each particular dimension separately. To show how it has happened that researches, very different at their point of departure, have, as regards one point of investigation, ended in nearly similar formulæ, the author proceeds to deduce his formula (VIII\*.) from the investigations of Bézout. Such a deduction, he conceives, might readily have been made by any one to whom it had occurred to make it; and the application of such a deduction, when once made, to problems in Combinations, would have been much too obvious to have remained long unnoticed.

Expressions of the form above considered are regarded by Bézout as of the nature of Differences; and the truth of this view of the subject may be shown in the following brief manner.

If  $\phi(x)$  generates  $\psi(u)$ ,  $[1-x^\alpha]\phi(x)$  will generate  $\psi(u)-\psi(u-\alpha)$ , which we may denote by  $\Delta_\alpha\psi(u)$ . Consequently  $[1-x^\beta][1-x^\alpha]\phi(x)$ , that is to say,

$$\left\{ \begin{array}{c} 1-x^\alpha+x^{\alpha+\beta} \\ -x \end{array} \right\} \phi(x),$$

will generate  $\Delta_{\alpha,\beta}^2\psi(u)$ ; and so on; the independent variable,  $u$ , undergoing, not uniform, but variable decrements,  $\alpha, \beta, \gamma, \&c.$

## L. Intelligence and Miscellaneous Articles.

### ON THE ARTIFICIAL PRODUCTION OF MINERALS, AND ESPECIALLY OF PRECIOUS STONES.

**M.** EBELMEN states that the first results which he obtained related to minerals of the family of Spinelles.

The method adopted by the author to effect the crystallization of these compounds, is based on the property which boracic acid pos-

seses of dissolving metallic oxides in the dry way, and the volatility of this acid at a high temperature. It occurred to him that by dissolving alumina and magnesia, mixed in the proportions which constitute spinelle, in fused boracic acid, and exposing the mixture in open vessels to the high temperature of a porcelain furnace, that the affinity of the alumina for the magnesia might cause the separation of a crystallized aluminate and the expulsion of the boracic acid. The proportions employed were about one part of fused boracic acid, and two parts of a mixture of alumina and magnesia, composed so as to constitute the compound  $\text{Al}^2\text{O}^3 \text{MgO}$ ; and from  $\frac{1}{100}$  to  $\frac{1}{200}$  of bichromate of potash were added to it. The ingredients, well-mixed, were placed on platina foil, in a cup of porcelain, and exposed to the highest temperature of the porcelain furnace of Sèvres. A product was obtained the surface of which was covered with crystalline facets, and the interior contained cavities sprinkled with crystals, the form of which was readily distinguishable with a glass. These crystals were rose-red, transparent, scratched quartz readily, and had the form of the regular octohedron without any modification. They were completely infusible by the blowpipe. These characters, combined with the composition of the crystals as deduced from synthesis, appear to M. Ebelmen sufficiently conclusive as to their identity with spinelle.

By substituting the equivalent of protoxide of manganese for magnesia, a crystalline product was obtained in large laminae, exhibiting the form of equilateral triangles or regular hexagons. The author considers these as constituting the manganeseian spinelle  $\text{Al}^2\text{O}^3 \text{MnO}$ , which has not hitherto been met with in the mineral kingdom.

Oxide of cobalt substituted for magnesia, equivalent for equivalent, yielded crystals of a black-blue colour, in regular octohedrons. They also scratched quartz, but not so readily as the two preceding.

In employing alumina and glucina in the proportions which constitute cymophane  $\text{Al}^2\text{O}^3 \text{GIO}$ , a mass covered with crystalline asperities of great splendour was obtained. This product scratched quartz and even topaz distinctly; it therefore possessed hardness comparable to that of natural crystallized cymophane.

Certain silicates, which are infusible by the heat of our furnaces, appear also to be produced by the same process. Thus, on fusing the elements of emerald with half their weight of boracic acid at the same temperature as in the preceding experiments, a substance is obtained which easily scratches quartz, and its surface presents a great number of facets, the form of which is the regular hexagon.

The author proposes to continue these experiments, but at present only states in addition, that it is possible to produce at temperatures lower than those obtainable in our furnaces, diaphanous crystals, the hardness and external characters of which are analogous to those of precious stones; and he also concludes that many mineral species may be formed at a lower temperature than that required for their fusion.—*Comptes Rendus*, August 16, 1847.

## ANALYSIS OF THE GRAY COPPER FROM MOURAÏA IN ALGERIA.

M. Ebelmen states that a copper mine, apparently of great importance, has been for some time worked at the foot of the defile of Mouraïa in Algeria. The veins are composed principally of carbonate of iron and gray copper ; the latter sometimes occurring in compact masses and sometimes in crystals, the prevailing form of which appears to be a rhombic dodecahedron, but with numerous modifications on the edges and angles.

The specimens received by M. Ebelmen for analysis contained a great number of very brilliant small crystals of gray copper, on a gangue composed of carbonate of iron and sulphate of barytes. These specimens were digested for some time in warm dilute hydrochloric acid, which dissolved the carbonate of iron without altering the gray copper, the crystals of which were then readily detached.

Qualitative experiments, conducted in the usual manner, showed that the ore contained sulphur, arsenic, antimony, copper, iron and zinc : lead, bismuth, and mercury were tried for, but not the smallest quantity was found. No notable quantity of silver could be detected ; and the fact that M. Berthier found 0·0008 in 1 part of the ore, shows that the silver is very irregularly interspersed through the veins.

For the quantitative analysis of this ore, M. Ebelmen employed, with a slight modification, the method proposed by M. H. Rose ; and taking the mean of several experiments, he obtained the following as the composition of this ore :—

Sulphur .....	27·25
Antimony .....	14·77
Arsenic .....	9·12
Copper .....	41·57
Iron .....	4·66
Zinc .....	2·24
	99·61

If the analysis of this ore be compared with that of gray copper from various localities, the greatest similarity will be found between it and that from Sainte-Marie-aux Mines, which gave M. H. Rose—

Sulphur .....	26·83
Antimony .....	12·46
Arsenic .....	10·19
Copper .....	40·60
Iron .....	4·66
Zinc .....	3·69
Silver .....	0·60
	99·03

## ANALYSIS OF KUPFERNICKEL.

M. Ebelmen states that this mineral comes from Ayer, in the valley of Annivier (H<sup>t</sup> Valais). It possesses the usual characters of Kupfernickel. It forms compact masses which are perfectly homogeneous, but exhibit no traces of crystals; the ore is mixed with laminar carbonate of lime, which is easily separated by dilute hydrochloric acid. Its density is 7.39.

The analysis was effected by treating the purified mineral with aqua regia. The sulphuric acid was precipitated by chloride of barium and the excess of barium by sulphuric acid. The arsenic acid was converted into arsenious acid by means of ebullition with sulphurous acid, and the arsenious acid was precipitated by sulphuretted hydrogen. The sulphuret of arsenic obtained was, after drying and weighing, analysed by aqua regia to obtain the sulphur; by heating another portion in a current of hydrogen, a minute residue of antimony was obtained. The liquor freed from sulphuret of arsenic was concentrated along with nitric acid, and precipitated by excess of ammonia; an abundant precipitate of peroxide of iron was formed, which retained a little nickel, as appeared from its colour.

It was redissolved on the filter by hydrochloric acid, and the liquor was then treated cold with carbonate of barytes. The peroxide of iron only was precipitated; the carbonate of barytes, with which it was mixed, was readily separated. The liquor containing the nickel was treated with sulphuric acid, and after filtration it was added to the ammoniacal solution of the rest of the nickel; this was precipitated by excess of potash, and after drying and calcining, it was weighed, and its quantity indicated that of the metallic nickel.

The ammoniacal liquor, afterwards treated with hydrosulphate of ammonia, yielded a slight black precipitate, which, collected, calcined and weighed, gave with borax the reaction of cobalt.

The results of the various experiments showed that the ore consisted of—

Arsenic .....	54.05
Antimony .....	0.05
Nickel .....	43.50
Cobalt .....	0.32
Iron .....	0.45
Sulphur .....	2.18
Gangue .....	0.20
	100.75

*Annales des Mines*, tome xi. p. 56.

## ON THE DEHYDRATION OF MONOHYDRATED SULPHURIC ACID.

M. Barreswil observes that anhydrous sulphuric acid has been hitherto prepared by distilling protosulphate of iron or dry bisulphate of soda. These two processes produce an anhydrous salt and sulphuric acid. The author states that he is not aware that an

attempt has ever been made to deprive concentrated sulphuric acid of spec. grav. 1·848 of its water, without previously causing it to enter into combination and form a salt. The same may also happen when monohydrated sulphuric acid is employed in the preparation of fluoboric and fluosilicic acids, which are considered as substances having great affinity for water.

The reaction which M. Barreswil employs he considers as extremely simple. He mixes anhydrous phosphoric acid with the sulphuric acid of commerce, and leaves them in contact, and the mixture is afterwards heated : the combination of the two acids produces an increase of temperature, and some acid vapours soon appear ; but this is prevented by proceeding cautiously, and keeping the acids in a freezing mixture : by distillation anhydrous sulphuric acid is disengaged, and vitreous hydrated phosphoric acid remains ; the distillation is effected in the same way as the Saxon acid.

A circumstance which struck the author in this operation, is the fact of the innocuousness of the mixture of monohydrated sulphuric acid and anhydrous phosphoric acid, with respect to organic matters, such as paper and cotton, which are instantaneously destroyed by the Saxon acid. The author considers this circumstance as a proof that the sulphuric acid in the mixture is not anhydrous, but becomes so when heat is applied.

Even if the reaction above described possesses interest in a theoretical point of view, M. Barreswil admits that as a manufacturing process it is unimportant, and will hardly be regarded as a ready method of obtaining anhydrous sulphuric acid. The high price of phosphorus, and the difficulty of preparing anhydrous phosphoric acid, are obstacles to the employment of the process.—*Comptes Rendus*, Juillet 5, 1847.

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#### OBSERVATIONS ON SILICA. BY M. DOVERI.

It results from the experiments detailed by the author—

1. That the alkaline silicates, when decomposed by acids, and particularly hydrochloric acid, deposit the greater part of the silica which they contain if the acid in excess be added drop by drop ; whereas the same quantity of acid added at once does not occasion the precipitation of the smallest portion of silica.
2. That silica, once precipitated, does not redissolve in acids, whatever may have been its origin, whether precipitated from an alkaline silicate by an acid, or from fluoride of silicium by water.
3. That weak acids, as the carbonic, sulphurous, boracic and the vegetable acids, decompose the alkaline silicates at common temperatures, and precipitate the silica either as a jelly or in gelatinous flocculi.
4. That very finely-divided silica, whether anhydrous or hydrated, is capable of decomposing the aqueous solutions of the alkaline carbonates, and dissolving in the solution at a boiling heat.
5. That silica precipitated at common temperatures from a solu-

tion of an alkaline silicate or from fluoride of silicium, is a hydrate of definite proportions, the composition of which may be represented by the formula  $\text{HO}_2\text{SiO}_3$ . This hydrate, when heated to  $212^\circ \text{ F}.$ , loses one equivalent of water, and is converted into another compound,  $\text{HO}_2\text{SiO}_3$ .

6. That when a solution of an alkaline silicate is treated with a metallic solution, a precipitate is formed, which is a mixture of hydrate of silica and a metallic silicate; the metallic silicate being entirely dissolved by the mineral acids, while the free silica remains undissolved.

7. That a limpid and very strong solution of silica in hydrochloric acid may be obtained by dissolving in this acid silicate of copper, and precipitating the copper by sulphuretted hydrogen.

8. That a solution of silica in hydrochloric acid, slowly evaporated under the receiver of the air-pump, gives hydrate of silica ( $\text{HO}_2\text{SiO}_3$ ) perfectly crystallized in very small transparent needles, grouped either in stars or tufts.—*Comptes Rendus, Juillet 19, 1847.*

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#### ON NITRIC MANNITE. BY M. SOBRERO.

Since the action of nitric acid on organic bodies has been studied, a number of substances of great interest to science have been discovered; but the arts have hitherto acquired only fulminating-cotton, the fate of which is as yet uncertain. Whilst the question as to cotton is under consideration, M. Sobrero announces to the Academy another body which is fulminating in the highest degree, resulting from the action of nitric acid upon mannite—the nitric mannite, the composition of which has been already given by MM. Flores Domonte and Ménard.

Fulminating mannite possesses the property of detonating by the stroke of a hammer with as much violence as fulminate of mercury, and produces, during its decomposition, sufficient heat to inflame gunpowder. As soon as the author was acquainted with this property, he set about to apply it, and prepared capsules with it instead of detonating mercury for the discharge of fire-arms, and a fowling-piece was discharged by it.

With respect to its use, the author has arrived at the following conclusions:—

1. Fulminating mannite must always be cheaper than fulminating mercury.

2. It is more conveniently prepared, and does not expose the workmen to the great danger which attends the manufacture of fulminating mercury.

It must be cheaper than fulminating mercury, because the price of manna is not very high; because in the preparation of mannite an uncryallizable residue is obtained, mixed with a little mannite, which may be employed in medicine and the veterinary art as a purgative; and because, according to the analyses of MM. Flores

Domonte and Ménard, the mannite, in becoming nitric mannite, must increase considerably in weight (from 100 to 225).

It is less dangerous in preparation and manipulation : in fact the preparation is merely accompanied with the disengagement of some vapour of nitric acid.

Fulminating mannite requires for detonation a violent blow between two hard bodies ; heat gradually applied to it fuses and afterwards decomposes it, but without detonation. In fact it may be placed on paper and touched with a red-hot coal, and fused without detonation ; the paper on which it is put may be burnt, and it is decomposed without detonation.

Lastly, fulminating mannite is decomposed by the blow of a hammer, without, as far as appears, producing nitrous vapours. It seems to be entirely decomposed into carbonic acid, water and azote ; besides which it keeps indefinitely without undergoing decomposition.—*Comptes Rendus*, Juillet 19, 1847.

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#### ON THE EXTRACTION OF SILVER.

BY MM. MALAGUTI AND DUROCHER.

From the numerous researches which the authors have made on a large series of specimens from different parts of Europe, they have inferred the general fact, that all metallic compounds which accompany or are found near argentiferous minerals contain more or less silver ; so that they deem it an established fact, that silver is probably one of the most widely-diffused metals in nature.

The researches of the authors have been made on sulphurets, arseniurets, arsenio-sulphurets, some metallic oxides, and even native metals. This fact being established, the mode in which the silver exists occupied their attention. As the subject appeared a difficult one, it was simplified by inquiring in what state the silver existed in galena, blonde and pyrites, and they supposed it could exist only in the native state, as chloride or sulphuret. Experiments appeared to show that in these sulphurets the silver is not in the metallic state ; and experiments still more numerous and decisive seemed also to prove that the silver could not be in the state of chloride ; and on this occasion they remarked a circumstance which has hitherto escaped the observation of chemists :—They found that all metallic sulphurets, properly so called, and even some arseniurets, possess the property of decomposing a certain quantity of chloride or bromide of silver. This decomposition is effected more or less slowly when contact is effected merely by water ; but it is produced much more rapidly, and in some cases even instantaneously, when the chloride or bromide of silver is in solution.

By comparative trials the authors succeeded in determining the decomposing power of a great number of sulphurets and several arseniurets. Thus—

100 of sulphuret of zinc decompose	3	of chloride of silver	
100 . . . . cadmium .. 14		....	
100 . . . . bismuth .. 2		....	
100 . . . . lead .. 5		....	
100 protosulphuret of tin .. $\frac{1}{2}$		....	
100 of bisulphuret of tin .. 30		....	
100 protosulphuret of copper .. 360		....	
100 arseniuret of antimony .. 120		....	
100 . . . . cobalt .. 166		....	

In operating with natural sulphurets, the authors remarked very considerable differences in their decomposing power. They attribute these differences to the presence of small quantities of sulphurets or arseniurets of very high decomposing power; and they suppose they may sometimes attach to the molecular condition of the bodies. They found, for example, that a very pure and well-crystallized blende from Königsberg possessed decomposing power equal to that of artificial sulphuret of zinc; while a blende equally pure and as well crystallized, but coming from Radna, had a decomposing power which was twice as weak, and yet these two blendes were of equal density.

The authors draw the following conclusions from the results of their experiments:—

All pure metallic sulphurets possess the power of decomposing, under certain circumstances, a given quantity of chloride of silver, and even of other insoluble chlorides. This power appears to be modified in some cases by the molecular condition.

The decomposition of chloride of silver by sulphurets may be effected,—1st, by double decomposition; 2nd, by reduction; 3rd, by simultaneous reduction and double decomposition.

Natural sulphurets sometimes exhibit very high absorbent powers, on account of the presence of minute quantities of foreign sulphurets or arseniurets, acting by the reduction of the chloride of silver.

The decomposing action of sulphurets is exerted proportionally on the bromide of silver, and it is but slightly appreciable on the iodide.

In these phænomena the solvent exerts no influence; for the same results are obtained, except as to time, by simple contact aided by water.

The general fact of the decomposition of insoluble chlorides by sulphurets appears then to render it probable that, in natural sulphurets, the silver is in the state neither of chloride nor bromide.

Having then shown the improbability of the presence of metallic silver or chloride in the natural argentiferous sulphurets, the authors are of opinion that it must exist in the state of sulphuret; but if this conclusion were correct, how does it happen that blende, pyrites and galena, do not yield silver to mercury? Is not the sulphuret of silver almost as readily acted upon by mercury as metallic silver itself? The authors propose shortly to communicate the second part of this inquiry to the Academy.—*Comptes Rendus*, Juillet 26, 1847.

## VANADIATE OF LEAD AND COPPER.

M. Dufrénoy presented to the Academy, in the name of M. Domeyko, Professor of Chemistry and Mineralogy in the college of San Yago, Chili, an account of this new mineral, which is composed of—

Oxide of lead .....	54·9
Oxide of copper.....	14·6
Vanadic acid.....	13·5
Arsenic acid .....	4·6
Phosphoric acid.....	0·6
Chloride of lead .....	0·3
	—
	88·5

*Comptes Rendus*, Mai 5, 1847.

## METEOROLOGICAL OBSERVATIONS FOR AUG. 1847.

*Chiswick*.—August 1, 2. Very fine: sultry. 3. Very fine: clear. 4. Very fine: densely overcast. 5. Rain. 6. Overcast. 7. Very fine. 8. Very fine: cloudy. 9. Cloudy: shower: clear. 10. Rain: showery. 11. Very fine. 12. Light clouds, with bright sun at intervals: clear at night. 13. Overcast: very fine. 14. Very fine: cloudy. 15. Cloudy: clear: lightning at night. 16. Rain. 17. Overcast. 18. Heavy rain. 19. Overcast: lightning at night. 20. Uniformly overcast: slight fog. 21. Slight fog: fine. 22. Overcast: rain: cloudy. 23. Cloudy: rain. 24. Cloudy: clear at night. 25. Very fine. 26. Overcast: very fine. 27, 28. Very fine. 29. Rain: very fine. 30. Very fine: cloudy. 31. Very fine: clear at night.

Mean temperature of the month .....	62°·68
Mean temperature of Aug. 1846 .....	64°·16
Mean temperature of Aug. for the last twenty years .....	62°·32
Average amount of rain in Aug. .....	2·41 inches,

*Boston*.—Aug. 1. Fine: 2 o'clock P.M. thermometer 83°. 2. Fine: rain P.M. 3, 4. Fine. 5. Cloudy: rain P.M. 6. Fine. 7. Fine: rain P.M. 8. Fine. 9, 10. Cloudy. 11. Cloudy: rain early A.M. 12. Cloudy. 13, 14. Fine. 15. Cloudy. 16. Cloudy: rain A.M. and P.M. 17. Cloudy: rain P.M. 18, 19. Cloudy. 20—25. Fine. 26. Cloudy. 27. Fine. 28. Rain. 29. Cloudy: rain early A.M.: rain P.M. 30, 31. Cloudy.

*Sandwich Manse, Orkney*.—Aug. 1, 2. Bright: clear. 3. Bright: cloudy. 4. Cloudy: drops. 5. Bright: cloudy. 6. Cloudy: fine. 7. Rain: fine. 8. Cloudy: rain. 9. Cloudy: fine. 10. Cloudy: rain. 11. Clear: showers. 12. Cloudy. 13. Clear: cloudy. 14. Cloudy: fine. 15. Bright: fine. 16, 17. Clear: fine. 18. Cloudy: fine. 19, 20. Cloudy. 21. Showers: rain. £2. Cloudy: showers. 23. Clear: showers: cloudy. 24. Cloudy: rain. 25. Cloudy. 26. Cloudy: rain. 27. Cloudy: clear. 28. Bright: showers: clear. 29. Showers. 30. Rain: showers. 31. Bright: rain.

*Applegarth Manse, Dumfries-shire*.—Aug. 1. Fair, but cloudy. 2. Fair and fine: shower early A.M. 3. One slight shower. 4. Rain early A.M. 5. Rain nearly all day. 6. Frequent showers. 7. Heavy showers and sun. 8. Rain. 9. Cloudy: cool: dry. 10. Heavy rain. 11. Fine A.M.: rain P.M. 12. Rain nearly all day. 13. Fair and fine. 14. Very fine. 15, 16. Very fine: heavy dew. 17. Fine, though cloudy. 18. Very fine. 19. Still fine, but dull. 20. Heavy showers. 21. Slight showers. 22, 23. Fine: clear. 24. Rain P.M. 25, 26. Fine, though cloudy. 27. Fine, though cloudy: a few drops. 28. Fine, though cloudy: one slight shower. 29. Fair and fine. 30. Fine: one slight shower. 31. Fine harvest day.

Mean temperature of the month .....	57°·15
Mean temperature of Aug. 1846 .....	61°·2
Mean temperature of Aug. for twenty-five years.....	57°·14
Average rain for twenty years .....	3·16 inches.

Days of Month.	Barometer.				Thermometer.				Wind.				Rain.				
	Chiswick.		Dumfries-shire.		Orkney, Sandwick.		Dunfries-shire.		Orkney, Sandwick.		Wind.		Rain.				
	Max.	Min.	9 a.m.	9 p.m.	9 a.m.	8½ p.m.	Min.	Max.	Min.	Max.	1 P.M.	Shore.	Boscombe.	Dunmifter.	Chiswick.	Orkney, Sandwick.	
1.	30-018	29-944	29-50	29-82	29-81	29-71	91½	46	70	67	59	63	55	s.	ssw.	'25	
2.	30-044	29-827	29-36	29-80	29-85	29-86	89	46	73	66½	52½	56	55	nw.	ww.	.....	
( 3.	30-009	30-003	29-48	29-86	29-88	29-82	77	38	62	64½	41½	53	n.	nw.	w.	-15	
4.	29-945	29-741	29-47	29-70	29-50	29-56	80	51	63-5	59	44	55	55	s.	'02	.....	
5.	29-640	29-504	29-17	29-41	29-59	29-44	72	54	59	51½	58	56	sw.	sw.	'28	'06	
6.	29-733	29-505	29-10	29-49	29-63	29-62	69	47	63	67	50	59½	56	nw.	ww.	'09	
7.	29-773	29-723	29-27	29-50	29-43	29-41	76	49	66	61	53	56½	55	s.	calm	'17	
8.	29-731	29-700	29-20	29-25	29-44	29-53	29-68	76	49	63	56	51	49½	sw.	n.	-10	
9.	29-876	29-751	29-23	29-61	29-63	29-72	29-69	66	44	58	61	49	52½	w.	calm	'22	
10.	29-881	29-808	29-40	29-60	29-63	29-58	29-60	65	48	55	60	43	55½	sw.	w.	.....	
( 11.	30-112	30-072	29-57	29-85	29-80	29-82	29-76	79	61	59½	65	46	59	56	s.	'05	'27
12.	30-110	30-088	29-54	29-78	29-94	29-69	29-83	86	58	68	61	56	59½	sw.	sw.	'09	
13.	30-253	30-189	29-68	30-14	30-28	30-11	30-27	81	49	68	66	44½	54	ne.	ww.	.....	
14.	30-316	30-276	29-84	30-30	30-37	30-40	79	52	65	68½	41	58	55½	s.	s.	.....	
15.	30-222	30-163	30-24	30-31	30-24	30-35	30-32	80	56	66½	45½	51	54	ne.	e.	'60	
16.	30-088	30-040	29-67	30-21	30-15	30-24	30-17	68	61	63	68½	46½	59	56	ne.	ne.	'05
17.	30-044	30-040	29-58	30-09	30-18	30-27	30-31	71	60	63	71	46	56	52½	ne.	'34	
18.	30-101	30-082	29-63	30-20	30-18	30-26	30-26	85	62	66	66	58½	55	ne.	n—s.	'79	
19.	30-119	30-016	29-67	30-14	30-01	30-14	30-14	90	55	64	71	47½	56½	57	ne.	'13	
20.	29-971	29-895	29-54	29-90	29-80	29-75	29-68	72	49	65½	70½	46	56½	53	ne.	.....	
21.	29-911	29-749	29-43	29-78	29-40	29-72	29-31	82	54	66½	62	49	55	54	sw.	'08	
22.	29-763	29-666	29-17	29-34	29-66	29-66	29-66	68	43	66	61	51	46	46	calm	'03	
23.	29-488	29-886	29-48	29-97	29-05	29-05	29-98	61	46	56	62½	41	51	50	calm	'41	
24.	30-124	30-075	29-70	30-10	30-07	30-07	29-96	69	49	61½	37½	56	54	ne.	w.	'07	
25.	30-113	30-071	29-68	29-95	30-02	30-00	29-97	74	50	59	61½	55	56½	ne.	se.	'09	
( 26.	30-227	30-146	29-69	30-12	30-11	30-11	30-06	72	43	62	63½	48	60	57	calm	'11	
27.	30-297	30-254	29-75	30-11	30-11	29-97	30-01	81	46	67	69	56½	63½	56½	calm	'03	
28.	30-305	30-197	29-77	30-20	30-12	30-09	30-10	81	55	69	49	57½	54	54	sw.	'41	
29.	30-145	30-097	29-64	30-10	30-09	30-07	29-98	75	44	62	65	50½	55	54	nw.	'06	
30.	30-065	29-976	29-49	29-90	29-78	29-80	29-73	69	53	57	59½	51	55	54	sw.	'16	
31.	30-009	29-951	29-48	29-88	29-83	29-81	29-56	67	42	61-5	65½	51	54½	53	sw.	'07	
Mean.	30-064	29-949	29-51	29-884	29-881	29-873	29-869	75-04	50-32	63-1	64-2	50-1	57-00	54-09	1-50	1-46	2-23-3-20

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[THIRD SERIES.]

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LI. *Researches on the Voltaic Arc, and on the influence which Magnetism exerts both on this Arc and on bodies transmitting interrupted Electric Currents.* By M. AUGUSTE DE LA RIVE, Professor in the Academy of Geneva, Foreign Member of the Royal Society, Corresponding Member of the Academy of Sciences at Paris, &c.\*

THE luminous voltaic arc occurring between two conducting bodies, each communicating with one of the poles of the pile, is not merely one of the most brilliant phænomena in physics, but, from the numerous aspects under which it may be regarded, it is also one of the most important.

As a source of light, this phænomenon, when exhibited in a vacuum, enables us to examine what influence this particular origin of the light employed may have in various optical experiments. Compared with the solar light, the light of the voltaic arc presents some curious differences and also resemblances. If, on the one hand, we find in it the seven coloured rays of the spectrum, on the other the black streaks are replaced by brilliant ones, and these are differently interspaced. In this field of inquiry, much, or rather all, yet remains to be investigated.

As a source of heat, the voltaic arc enables us to study the fusion and solidification of even the most refractory bodies *in vacuo*, and consequently under circumstances exempting them from oxidizing action and other chemical influences, which usually result from the application of a high temperature in atmospheric air. It likewise allows us to determine the effects produced upon bodies at a high temperature, by various gases or vapours, distinct from those which enter into the composition of atmospheric air, and at different degrees of density.

As an electro-chemical power, the voltaic arc may be ap-

\* From the Philosophical Transactions for 1847, part i.; having been received by the Royal Society Nov. 26, 1846, and read Jan. 7, 1847.

plied so as to submit to the electrolizing action of the electric current gaseous media, which, from some experiments already made, appear capable of decomposition by this process.

As a mechanical power, the voltaic arc, by bringing bodies into a state of minute division, and impressing upon them, in this state, a tendency to motion, places them in a favourable condition for the study of their molecular constitution, and of the relations which connect this constitution with electricity and magnetism. The struggle that takes place between cohesion and the expansive force of the electric current, the reduction of matter to the molecular state, and the form and nature of the deposits resulting therefrom, are so many phænomena capable of throwing light on the obscure subject of molecular physics.

The few preceding remarks suffice to give some idea of the extent of an investigation embracing the whole range of experimental research on the voltaic arc under its various aspects, which I am far from pretending to have attempted. I shall confine myself at present to a few details, and especially to such as exhibit the action of magnetism on the voltaic arc, and on those bodies which transmit interrupted currents. I shall begin by describing some particular phænomena which I observed during my study of the voltaic arc under various circumstances, while employing different substances as electrodes, both in the air and in a vacuum; I shall then proceed to examine the action of a powerful electro-magnet on this voltaic arc, and I shall conclude by describing some remarkable experiments also illustrating the influence of magnetism on conducting bodies, of whatever nature, traversed by interrupted currents.

### § 1. *Some Phænomena concerning the Voltaic Arc.*

Davy was the first who produced the phænomenon of the voltaic arc with two points of charcoal. More recently, Messrs. Grove\* and Daniell† employed with success the points of different metals, and arrived at interesting results: I also published some experiments I made on the voltaic arc ‡ in 1841. Subsequently, MM. Fizeau and Foucault observed some remarkable facts of the same kind on the occasion of an investigation into the intensity of the light emitted by charcoal in the experiment of Davy §. The researches made up to the present time, have already led to many results, of which I shall consider only the most important.

1. That the voltaic arc may be produced, a pile of greater tension is required than that which is necessary for the ordi-

\* *Bibl. Univ.* June 1840, i. 27. p. 387. † *Arch. de l'Elect.* tom. i. p. 462.

‡ *Arch. de l'Elect.* tom. i. p. 262.

§ *Ibid.* tom. iv. p. 311.

nary calorific and electro-chemical phænomena. The necessity of this condition proves the great resistance presented to the passage of the electric current by the minutely divided matter, whatever it may be, which connects the two poles.

2. The luminous arc cannot exist, unless contact be previously made between the electrodes, and unless these, or at least one of them, be terminated at the point of contact by points fine enough to produce in them an increase of temperature. When this increased temperature is once produced, we may, by separating the electrodes gradually and with precaution from each other, obtain the luminous arc, the length of which will depend on the intensity of the pile. Daniell discovered the important fact, which was confirmed by M. Van Breda in a very recent investigation inserted in the *Comptes Rendus de l'Académie*\*, that without contact having taken place, the luminous arc may be produced between two electrodes placed very near together, by causing the discharge of a Leyden jar to pass between them: this is owing to the discharge being always attended by the transference of highly diffused matter, which closes the circuit during the instant of time necessary for the formation of the arc.

3. The enormous elevation of temperature which accompanies the production of the luminous arc, is also manifested in the electrodes, especially in the positive ones, which become much more strongly heated than the negative.

4. Matter is thus transported from the positive electrode to the negative, a fact which may be verified with electrodes of all kinds, but particularly with those of charcoal.

5. The various phænomena presented by the voltaic arc, are modified to a greater or less extent by the nature of the electrodes and by that of the surrounding medium. Thus Mr. Grove adduces facts from which it appears that the presence of oxygen is necessary in most cases to produce a very luminous and brilliant arc. It results also from his experiments, as well as those of other philosophers, that when two different substances are made use of for the electrodes, it is not a matter of indifference which of the two is placed at the positive pole.

I now proceed to my own researches. I commenced by studying the production of a luminous arc between a plate and a point of the same material in air, and *in vacuo*. By means of a micrometer screw I was able to make the point recede from the plate very gradually, and judge of their mutual distance with great precision. The limit of distance beyond which the luminous arc ceases to appear, is constant for the

[\* See also p. 538 of the December Number of this Journal for 1846.]

same plate and the same point: when, however, the plate communicates with the positive pole, it is in general double that which it is when the point communicates with the same pole. But in proportion as the strength of the pile is greater, the difference is so much the smaller.

With respect to the absolute amount of this distance, it is very variable, depending on the strength of the pile, on the nature and molecular state of the electrodes, and on the time occupied in the experiment. Thus, with a Grove battery composed of fifty pairs of plates sixteen square inches in surface, it is two or three times greater than with a pile of seventy elements of two or three square inches. With metals easily fused or oxidized, as zinc and iron, it is much greater than with platinum or silver. The duration of the phænomenon influences the result, inasmuch as the high temperature of the electrodes allows them to be drawn asunder to a greater distance without breaking the arc. The same effect may be produced by heating them artificially, by means of a spirit-lamp. It is evident from what I have said that the length of the luminous arc has a relation to the greater or less facility which the substances composing the electrodes possess of being segregated, a facility which may depend upon their temperature diminishing their cohesion, upon their tendency to oxidize (which produces the same effect), upon their molecular state, and lastly upon their peculiar nature. Carbon derives from its molecular constitution, which renders it so friable, the property of being one of the substances which produces the longest luminous arc.

The deposits of the transported matter, form upon the plate, when it is negative and the point positive, a species of very regular ring, the centre of which is the projection of the point upon the plate. This takes place equally, whether the plate be vertical or horizontal, plainly indicating a determinate direction in the transfer of the substance from the positive to the negative electrode; in the air and with metallic electrodes, the deposits always consist of the oxidized dust of the metal, of which the positive electrode is composed.

I shall here enter into some details. A plate and a point of platinum have been used as electrodes in a vacuum, in air and in hydrogen. In a vacuum with a Grove battery of fifty pairs of plates, which had previously been used, I had only a very feeble effect, and particularly when the plate served as the positive electrode. The point was hardly removed a millimetre\* from the plate when the arc broke; to re-establish it, it became necessary to renew the contact between the point

\* 1 millimetre = 0.03937 inch.—*Trans.*

and the plate, by touching another point of the plate, the first point which was touched appearing to have undergone such a modification as to prevent the re-formation of the arc. The same effect is produced when the experiments are made in the air, but it ceases when the power of the battery is increased: this is probably due to an augmentation of cohesion consequent on the increase of temperature in that part of the plate which acts as the positive electrode. Besides, when the experiment is made in air, the voltaic arc is more marked and of greater length than when it is made *in vacuo*, at least if the battery be weak; for when the battery is powerful, composed, for example, of fifty pairs of plates freshly charged, it appeared to me that the contrary obtained. I did not, however, perceive any great difference; but the vacuum in which I experimented was far from being perfect; it was that of a pneumatic pump, enclosing therefore highly rarefied air.

In the latter case, that is to say, with the pile composed of fifty pairs strongly charged, and in highly rarefied air, a bluish spot, perfectly circular and presenting the appearance of a coloured ring of Nobili, was formed on the plate of platinum when it served as the positive electrode. The same spot appeared in atmospheric air, but its diameter was one-half less, and its colours much less vivid. In hydrogen, no coloured spot was formed; its formation is therefore evidently the result of the oxidation of the platinum at a high temperature when acting as a positive electrode in the ordinary atmosphere, and still more so, perhaps, in rarefied air\*. When the same plate of platinum was made use of as a negative electrode, the point being positive, it became covered with a white circular spot, formed of a vast number of minute grains of platinum, which, having been raised to a high temperature, remained adhering to the surface. The white spot, like the blue one, was much larger in rarefied air than in a vacuum. If the experiment be prolonged for a minute or two when the plate is negative, the rod of platinum terminating in a point, which is positive, soon becomes highly incandescent; its end is fused and falls on the plate in the form of a perfectly spherical globule. When the plate is positive and the point negative, the latter is less heated, and does not become fused; but the plate, unless it be very thick, is liable to be perforated: besides, as may easily be

\* This effect may possibly have been owing to the action of the oxygen brought by the voltaic current into that particular state which Schönbein first described under the name of *ozone*. Indeed, in this state the oxygen may attack those metals which are supposed to be inoxidizable; and M. Marignac and I have shown that this may be effected by causing a succession of electric discharges to pass through the oxygen, even when very dry, with which the phænomenon of the voltaic arc has a great resemblance.

imagined, the phænomenon lasts much longer in the latter case. The light is less brilliant, but it is accompanied by a reflexion of a superb blue, which may be seen when the experiment is made in the interior of a bell, whether the air be rarefied or not. This blue reflexion is observed on the side of the bell, and is to be seen whatever may be the nature of the electrodes, or the colour of the light to which these give rise in the centre of the bell; only when this central light is very brilliant, it becomes slightly paler by the effect of contrast.

I substituted for the platinum point a point of coke, but the plate of platinum remained; this being positive and the point negative, I obtained a luminous arc more than double the length of the arc produced by the point of platinum. With respect to the arc, instead of its being a cone of light, having its base on the plate and its apex at the point, as was the case when the latter was platinum, it was composed of a multitude of luminous jets diverging from different points of the plate, and tending to various parts of the point of coke. This fact shows clearly the influence that may be exercised by the negative electrode, the function of which is very far from being a merely passive one. Let me add, that although the strength of the pile was precisely the same as when the point was of platinum, not only was the luminous arc much longer with the point of coke, but the heat developed in the plate of platinum was so much greater that it was soon melted and perforated. The coke being positive and the plate negative, the length of the arc was less than in the preceding case, and particularly so in air, where it was sensibly less than in a vacuum. The heat generated was however still very great, the point of coke becoming quickly incandescent throughout. I ought to add, that with the point of coke, the luminous arc was so brilliant that the blue light which I have mentioned almost entirely disappeared, which was not the case with any other kind of point.

Leaving the plate of platinum, I adjusted a zinc point. The effects were most brilliant, but of short duration, the point speedily melting. In common air, a deposit of white oxide was precipitated upon the platinum plate; in highly rarefied air (the vacuum of an air-pump), a black deposit was formed: in both cases it communicated with the positive pole. An iron point being substituted for that of zinc, equally produced in common air a brownish-red deposit of oxide of iron, and in rarefied air a deposit of black oxide.

I call the attention of chemists to these two facts, as well as that of the oxidation of the platinum at a high temperature in rarefied air. They appear to prove the influence which the state of greater or less density of the surrounding oxygen may

exert on the phænomenon of oxidation and on the nature of the oxide formed. A plate and a point of soft iron were used as positive and negative electrodes, both in a vacuum and in the atmosphere ; the same results appeared with a plate and a point of silver, a plate and a point of copper, and a plate and point of argentane\*. The blue light was perceived in all the experiments ; coloured circles were likewise seen on all the plates when they had acted as positive electrodes in rarefied air. The silver and copper plates presented in this case very decided cavities, caused by the passage of the matter from the positive to the negative pole. The points became incandescent throughout when they served as positive electrodes ; whereas when negative, they were heated only at their extremities. The copper point when positive became isolating at its extremity, and it was necessary to excite it by friction in order to renew the experiment. This circumstance is probably attributable to the formation of a thin film of oxide. The point and plate of copper gave out a luminous arc of a beautiful green light, which contrasted in a remarkable manner with the blue reflexion visible in this, as in the other experiments. Mercury was likewise employed, both as a positive and negative electrode. In a vacuum as well as in atmospheric air, the luminous effect was most brilliant. The mercury was excessively agitated, rising up in the form of a cone when it was positive, and sinking considerably below the positive point when it was negative. The quantity of vapour thrown off by the mercury during this experiment filled the bell so quickly that it was not easy to observe the details.

I shall terminate this section by stating a fact which appears to me to be important ; it is the influence which the nature of the metallic points forming the electrodes exercises on the temperature which they acquire in relation to the production of the voltaic arc. If the two points are of the same metal, both platinum, or both silver, the positive one alone becomes incandescent throughout its whole length. If the silver point be positive and that of the platinum negative, the latter becomes incandescent, and the silver one is much less heated. Thus, when the voltaic arc is formed, the circuit must be regarded as completed, and then it is those parts of the circuit which present the greatest resistance to the current which become the hottest ; at first it is that portion forming the arc itself, and then, in the rest of the circuit, the metal which is the worst conductor. But if the conductors be of the same material on both sides of the arc, or if there be only a slight

\* An alloy of copper and nickel : also known by the names of *pachsong* and *melchior*.

difference of conductibility between them, then the development of heat, instead of being uniform, as it might appear it ought to be, is much greater on the positive side. This important fact evidently proves that this portion of the circuit has to resist a much more energetic action than that which the other side experiences; a fact which is confirmed by the molecular segregation accompanying this action at the positive electrode. This want of resemblance in the phenomena presented by the two electrodes, although placed in conditions entirely symmetrical, deserves to be taken into serious consideration, for it may throw light upon the nature of the electric current, and upon the link which unites it with the molecular state of the bodies through which it is transmitted.

### *§ 2. Influence of Magnetism on the Voltaic Arc.*

Davy was the first who observed that a powerful magnet acts upon the voltaic arc as upon a moveable conductor, traversed by an electric current; it attracts and repels it, and this repulsion and attraction manifests itself by a change in the form of the arc. Even the action of the magnet may, as I have found, break the arc by too great an attraction or repulsion exerted upon it, causing the communication which the transmitted particles establish between the electrodes to cease.

The action which I have just mentioned is not the only one which magnetism exerts on the voltaic arc. I have already stated the curious fact, that if two points of soft iron acting as electrodes, be both placed within a helix formed of thick copper wire of several coils, the voltaic arc developed between the two points of iron ceases the moment a strong current is passed through the wire of the helices, and reappears if this current be arrested before the points have become cold. The arc cannot be formed between the two iron points when they are magnetized, whether by the action of the helices, or by that of a powerful magnet, unless they be brought much nearer to one another, and the appearance of the phænomenon is then entirely different. The transported particles appear to disengage themselves with difficulty from the positive electrode, sparks fly with noise in all directions, while in the former case it was a vivid light without sparks, and without noise, accompanied by the transfer of a liquid mass, and this appeared to be effected with the greatest ease. It is of little moment with respect to the result of the experiment, whether the two rods of magnetized iron present to that part of their extremities between which the luminous arc springs, the same magnetic poles or different poles.

The positive electrode of iron, when it is strongly magnet-

ized, produces, the moment that the voltaic arc is formed between it and a negative electrode of whatever nature, a very intense noise, analogous to the sharp hissing sound of steam issuing from a locomotive engine. This noise ceases simultaneously with the magnetization.

For the purpose of better analysing these different phænomena, I placed an electro-magnet of large dimensions and great power in such a manner as to enable me to place on each of its poles, or between them, different metals destined to form one of the electrodes of the pile, while one point of the same metal, or another substance, acted as the other electrode. I have alike employed as electrodes, placing them in the same circumstances, two points of the same metal or of different metals. The following are the results which I have obtained. A plate of platinum was placed on one of the poles of the electro-magnet, and a point of the same metal was placed vertically above it; the voltaic arc was produced between the plate and the point, the plate being positive and the point negative. As soon as the electro-magnet was charged, a sharp hissing was heard; it became necessary to bring the point of the plate nearer to enable the arc to continue, and the bluish circular spot which the platinum plate presented, became larger than when the experiment was made beyond the influence of the electro-magnet. The plate was made negative, and the point positive; the effect was then totally different; the luminous arc no longer maintained its vertical direction when the electro-magnet was charged, but took an oblique direction, as if it had been projected outwards towards the margin of the plate; it was broken incessantly, each time accompanied by a sharp and sudden noise, similar to the discharge of a Leyden jar. The direction in which the luminous arc is projected, depends upon the direction of the current producing it, as likewise on the position of the plate on one or other of the two poles, or between the poles of the electro-magnet. A plate and a point of silver, a plate and a point of copper, and generally a plate and a point of any other metal, provided it be not metal too easily fused, present the same phænomena.

Copper, and still more silver, present a remarkable peculiarity. Plates of these two metals retain on their surfaces the impression of the action that took place in the experiments just described. Thus, when the plate is positive, that portion of its surface lying beneath the negative point presents a spot in the form of a helix; as if the metal melted in this locality had undergone a gyratory motion around a centre, at the same time that it was uplifted in the shape of a cone towards the

point. Moreover, the curve of the helix is fringed throughout by minute ramifications, precisely similar to the tufts which mark the passage of positive electricity in a Leyden jar. When the plate is negative and the point positive, the marks are totally different, being merely a simple point, or rather a circle of a very small diameter, whence proceeds a line more or less curved, forming a kind of tail to the comet, of which the small circle might be the nucleus: the direction of this tail depends upon the direction in which the luminous arc has been projected.

When, instead of a plate and a point, two points are used for electrodes, it is evident that no visible trace of this phænomenon can be obtained; but both the sharp hissing and the detonations may be produced, which latter are sometimes so loud as to bear a resemblance to distant discharges of musketry. For this the electro-magnet must be very powerful, and the current which produces the arc very intense. I had observed that when I took for a positive electrode a point of platinum, and for a negative electrode a point of copper, and placed them between the two poles of the electro-magnet, the production of the voltaic arc between the two poles was accompanied by a sharp hissing noise; whereas in the opposite case, the copper being positive, and the platinum negative, the detonations were heard, attended by a frequent breaking of the arc. On examining this phænomenon more closely, I perceived that the fact I have just mentioned was due to the platinum becoming heated much more rapidly than the copper when they were employed as electrodes in producing the voltaic arc; and I have satisfied myself that in order to obtain the hissing sounds, it is necessary that the positive electrode should be at a sufficiently high temperature to experience a commencement of liquefaction; for without this condition, only a series of detonations are heard. The hissing would be the result of the easy and continuous transport of matter more or less liquefied from the positive electrode, whilst the detonations would be the effect of the resistance opposed by the same matter to the disintegration of its particles when it is not sufficiently heated. Numerous experiments made with metallic points, whether of the same or different natures, as silver, iron, brass, as also platinum and copper, some of which become heated sooner than others under the same circumstances, have quite confirmed me in this view of the subject. It is merely necessary to be careful, in order to produce the hissing noise, to maintain as much as possible the continuity of the arc when once the positive electrode becomes incandescent; while, on the other hand, to obtain the detonations, one of the

electrodes must be held in the hand, and then the arc frequently made and broken without waiting till the metallic points acquire too high a temperature.

It remains now to be considered why the influence of powerful magnetism, such as that exerted by the electro-magnet, is necessary for the production of these sounds, which are not heard in the ordinary experiment of the voltaic arc. This can arise only from the change which the magnet produces in the molecular constitution of the matter of the electrode, or rather in the highly diffused matter which forms the voltaic arc. This action is besides shown by the shortening of the arc, and by the remarkable difference which it presents in its appearance; it is therefore not surprising that it should also be capable of producing a phænomenon such as sound, which essentially depends on the variations in the molecular state of bodies. This view of the subject appears to me to deserve very particular attention: the results at which I have arrived, in pursuing it more closely, form the subject of the following section.

### § 3. *Influence of the permanent action of Magnetism on conducting bodies traversed by interrupted electric currents.*

Faraday's brilliant discovery of the action exerted by magnetism on a ray of polarized light, when that ray traverses a transparent body submitted to the action of a powerful electro-magnet, had no sooner been announced by its illustrious author, than the majority of philosophers saw in it a proof that magnetism, when at a high degree of intensity, has power to modify the molecular constitution of all bodies. They consequently attributed the phænomenon observed by Faraday, not to the direct action of the electro-magnet on the polarized ray, but to the modification effected by this action on the molecular constitution of the substance traversed by the ray. I was of this opinion, and communicated it to Mr. Faraday, who alludes to it in his memoir. Desirous, however, of founding this opinion on facts of a different kind, I asked myself if it were not possible to find in the electric current, an agent capable of performing the same function for opaque conducting bodies that polarized light does for transparent ones. I had stated in my paper on the sound emitted by iron wires traversed by interrupted electric currents, that the nature as well as the intensity of the sounds were singularly modified by the molecular state of the wire submitted to the experiment. I had particularly mentioned the influence of temper and annealing, of greater or less tension, and of temperature. I had shown that iron wire, when under the influence of an action which renders it magnetic, does not emit the same sound as

when it is in its natural state. Finally, by modifying, through the agency of heat, the molecular arrangement of some metals, such as platinum and brass, I had succeeded in obtaining from them, during the passage of the interrupted current, sounds, which, though feeble, were yet distinct.

The preceding reflexions tended to confirm me in my opinion, that sounds produced under the influence of magnetism in the experiments on the voltaic arc, are owing to a molecular modification effected by the action of the magnet, and the more so inasmuch as the voltaic arc may be regarded as produced by a succession of interrupted currents, following each other with extreme rapidity, rather than by a perfectly continuous current. I accordingly took bars of other metals besides iron, as of tin, zinc, lead, bismuth, &c. I placed them on the poles of the electro-magnet, and I caused an interrupted current from a Grove's battery of from five to ten pairs to traverse them. They emitted no sound as long as the electro-magnet was not magnetized; but as soon as it was, sounds were very distinctly heard, composed of a series of strokes corresponding to the interruptions of the current, and analogous to that produced by a toothed wheel. The bars were eighteen inches long, and from nine to ten lines square. Rods of copper, platinum, and silver produced a similar effect; a rod of iron did not emit a much louder sound under the influence of the magnet than it did when not exposed to this action.

What appeared to me most remarkable was, to find lead, a body so little elastic, yield a sound as powerful as those proceeding from the other metals, when placed under the same circumstances. The position of metallic bars with respect to the poles of the electro-magnet did not in any way modify the result of the experiment; they might be placed axially, that is to say, in the direction of the poles, or equatorially, that is, across the poles; the effect remained the same, being merely weakened as the distance between the bar and the poles increased. In order to hear the sound distinctly, when not very powerful, it was sufficient to establish a communication between the metallic bar and the ear by means of a wooden rod. In this manner the sound was not unfrequently heard prolonged some seconds, though growing constantly feebler, until it ceased entirely, after the source of magnetism had been withdrawn from the electro-magnet. Mr. Faraday has remarked an analogous fact in the action of the transparent medium on the polarized ray, an action which does not cease immediately with the magnetism of the electro-magnet. Is this prolongation owing to the magnetization of the electro-magnet not ceasing in a sudden manner; or to its return to its primitive

molecular state not taking place instantaneously in the substance submitted to its action? This question I am unable to decide. I incline, however, rather to the latter of these explanations, seeing that the effect is not equally perceptible in all bodies, and that it is, for example, more sensible in a bar of bismuth than in one of copper.

It is needless to remark that the calorific action of the current could not have any influence on the production of the phænomenon, since there could have been no development of heat, on account of the dimension of the bars compared with the force of the current. Besides, if the expansion arising from the heating of the body traversed by interrupted currents had caused the sound, the effect would have been produced equally, whether the bar had been under the influence of the magnet or not. This last remark applies equally to the following experiments, as to the preceding.

The intensity of the sound appears to depend much less on the nature of the substance submitted to the experiment, than on its form, its volume, and its mass. Tubes of platinum, of copper, and of zinc, emitted more marked sounds than massive cylinders of the same metals. I wound a leaden wire in the form of a helix round a cylinder of wood; I did the same with a very fine platinum wire, and also with copper, zinc, and tin wires, taking care to place the coils of the helices so far apart that each should be isolated. Placed like bars and tubes, whether in the direction of, or across the poles of the electro-magnet, these helices emitted very powerful sounds when, the electro-magnet being charged, they were traversed by the interrupted current. It was particularly surprising to hear the lead wire emit so strong a sound. A helix constructed with copper wire, covered with silk, and composed of several coils wound round each other, emitted a very intense sound; it also emitted one, but much feebler, under the action of the electro-magnet.

It is almost needless to remark, that in all these experiments an ordinary magnet produces the same effect as an electro-magnet. But what is more interesting, is to replace the action of the electro-magnet by that of a helix traversed by a strong continuous current, in the axis of which helix is placed the bar, the tube or the coiled wire, through which the interrupted current is transmitted. Experiments have shown me that in this case the results are the same; the intensity of the sounds is not very different, especially when tubes and wires coiled as helices are used.

If, between the exterior helix and the metal submitted to the action, a tube of soft iron is placed, the effect is a little

heightened : it is neither increased nor lessened when the tube is of copper, only in this case another sound is heard which seems to proceed from the copper tube. This tube, however, is not traversed by a current, but it is probably acted upon by the currents of induction, which the interrupted currents traversing the conductor placed in the axis of the helix produce in it. I constructed a double helix formed of two thick copper wires covered with silk and coiled, each forming several circumvolutions, the one exterior to the other. In making a continuous current pass through the exterior wire, and an interrupted current through the interior one, I heard a remarkably intense sound. In the reverse case, the sound existed, but was much weaker. This fact is evidently connected with the known property of helices traversed by electric currents exercising scarcely any magnetic influence exteriorly, whilst in the interior this action is very energetic.

Metals and solid bodies are not the only substances which produce the phænomena I have just described ; all conducting bodies, whatever may be their state or their nature, appear to be capable of producing them. Thus, I have observed them with pieces of charcoal of all kinds and shape. Mercury also produces them in a very marked manner. I have inclosed mercury in a tube of glass an inch in diameter, and ten inches long : the tube was completely full and closed with care, so that the mercury could have no motion. As soon as it was traversed by an interrupted current, transmitted by means of two platinum wires, and the electro-magnet or the helix was made to act upon it, a sound was heard remarkable for its intensity. When the mercury was placed in an open trough, instead of being inclosed in a tube, it likewise produced a sound, and in addition there was seen on its surface an agitation or vibratory motion, very different from the gyratory motion observed by Davy, which appears under the influence of the poles of a magnet when traversed by a continuous current.

Dilute sulphuric acid, and what is even better, salt water, were successively put in a capsule of platinum placed on one of the poles of an electro-magnet. A point of platinum immersed in the liquid, served, together with the capsule, to send an interrupted current through it. A sound was again heard, but less distinct, on account of the noise produced by the disengagement of the gas : still it was so clear that no doubt could be entertained of its existence.

It may perhaps be thought that in the experiments I have just described, the sounds are produced by the mechanical action of attraction or repulsion exerted by the electro-magnet

on the substance traversed by an interrupted current, and that, consequently, magnetism has no more share in the phænomenon than a finger might be supposed to have, when pressing on a sonorous cord. The simple description of the experiments shows this interpretation to be inadmissible. In the first place, the sound is the same with the wires in a helix, whether these wires be stretched or not, or whether they be of lead, platinum, or brass. Besides, how could this account for the sound produced in large masses, especially in liquids, such as mercury, and for the fact, that the position of the conductor traversed by the interrupted current with regard to the poles of the electro-magnet does not exert any influence on the phænomenon? Further, it must be remarked that the sound in question is not a musical sound, such as would be produced by a string or mass made to vibrate by a cause acting exteriorly at its surface; it is a series of sounds corresponding exactly to the alternations of the passage of the current; like a species of collision of the particles amongst themselves. Thus, the phænomenon is molecular; and it leads to the demonstration of two important principles.

The first principle is, that the passage of the electric current modifies, even in solid bodies, the arrangement of the particles; a principle which I have already deduced from the experiments contained in my preceding memoir on this subject. The second principle is, that the action of magnetism, under whatever form it may be exerted, modifies alike the molecular constitution of all bodies, and that this modification lasts as long as the cause producing it endures, and only ceases with it. What is the nature of these two modifications? This is what we must endeavour to investigate and to ascertain. I purpose to engage in this inquiry, and indeed I have already made some attempts of which it would, however, be premature to give any account. I shall confine myself at present to a single remark, which does not appear to me to be devoid of interest: it is, that the influence of magnetism on all conducting bodies seems to impress on them, as long as it lasts, a molecular constitution similar to that which iron, and generally all bodies susceptible of magnetism possess naturally; for it develops in them the property of producing, when traversed by interrupted currents, sounds identical with those emitted also by iron and other magnetic bodies when transmitting these currents, but produced in these last without requiring the action of a magnet.

**LII. Analyses of the Ashes of Rough Brown Sugar and Molasses.** By THOMAS RICHARDSON\*.

DURING some inquiries which I had occasion to make in the manufacture of an artificial manure for the sugarcane, it was necessary to know the composition of the ash of coarse brown sugar and molasses as imported into this country. The results may be interesting to some of the readers of your Journal.

**I. Rough Brown Sugar.**

206·48 grs. in its ordinary state left 2·74 grs. ash = 1·33 per cent. 143·05 grs. of ash furnished 18·16 grs. silica, and 4·75 grs. carbonic acid.

28·61 grs. of ash furnished 8·43 grs.  $\text{SO}_3 \text{BaO} = 2\cdot89$  grs. sulphuric acid.

28·61 grs. of ash furnished 0·19 gr. oxide of copper.

28·61 grs. of ash furnished 1·95 gr. peroxide of iron.

28·61 grs. of ash furnished 7·00 grs.  $\text{CO}_2 \text{CaO} = 3\cdot92$  grs. lime.

28·61 grs. of ash furnished 7·81 grs.  $\text{PO}_5 2\text{MgO} = 2\cdot86$  grs. magnesia.

16·12 grs. of ash furnished 7·36 grs.  $\text{Cl}_2 \text{Ag} = 1\cdot96$  gr. chlorine.

28·61 grs. of ash furnished 28·61 grs. chlorides of alkalies, and this yielded 33·88 grs. of the double chloride of platinum and potassium = 10·34 grs. chloride of potassium = 6·53 grs. potash, leaving 4·16 grs. chloride of sodium = 2·20 grs. soda. The ash also contained a trace of oxide of manganese.

The result of the analysis is therefore—

Potash . . . . .	22·84
Soda . . . . .	7·69
Lime . . . . .	13·69
Magnesia . . . . .	10·00
Peroxide of iron . . . . .	6·11
Oxide of copper . . . . .	·66
Oxide of manganese . . . . .	trace
Sulphuric acid . . . . .	10·12
Silica . . . . .	12·68
Carbonic acid . . . . .	2·32
Chlorine . . . . .	12·20
	98·31

\* Communicated by the Author.

Omitting the carbonic acid and combining the chlorine with the sodium and potassium, we obtain the following composition in 100 parts:—

Potash . . . . .	19·42
Lime . . . . .	14·67
Magnesia . . . . .	10·72
Peroxide of iron . . . . .	6·55
Oxide of copper . . . . .	·71
Oxide of manganese . . . . .	trace
Chloride of potassium . . . . .	8·03
Chloride of sodium . . . . .	15·46
Sulphuric acid . . . . .	10·85
Silica . . . . .	13·59
	100·00

## II. Molasses.

Great difficulty was experienced in incinerating the bulky charcoal mass left by boiling down the molasses. Part of the oxide of iron and sulphuric acid were decomposed; and this accounts for the excess in the analysis, as these substances were obviously in part twice estimated. 477·77 grs. left 17·21 grs. ash = 3·60 per cent.

64·27 grs. of ash furnished 6·46 grs. carbonic acid.

64·27 grs. of ash furnished 8·65 grs. charcoal, containing ·55 gr. peroxide of iron and ·26 gr. lime.

64·27 grs. of ash furnished 1·02 gr. silica.

21·423 grs. of ash furnished ·28 gr. peroxide of iron.

21·423 grs. of ash furnished 3·83 grs.  $\text{CO}_2 \text{CaO} = 2\cdot14$  grs. lime.

21·423 grs. of ash furnished 5·34 grs.  $\text{PO}_5 \text{MgO} = 1\cdot95$  gr. magnesia.

21·423 grs. of ash furnished chlorides of alkalies 14·91 grs., and this gave chlorides of platinum and potassium 32·88 grs. =  $\text{Cl}_2 \text{K}$  10·34 grs., leaving  $\text{Cl}_2 \text{Na}$  4·57 grs., = potash 6·53 and soda 2·42 grs.

12·62 grs. of ash furnished 2·38 grs.  $\text{SO}_3 \text{BaO} = 1\cdot818$  gr. sulphuric acid.

18·405 grs. of ash furnished 9·92 grs.  $\text{Cl}_2 \text{Ag} = 2\cdot453$  grs. chlorine.

The ash also contained traces of oxides of copper and manganese.

Collecting these results we obtain the following composition:  
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Potash . . . . .	30·50
Soda . . . . .	11·30
Lime . . . . .	10·42
Magnesia . . . . .	9·13
Peroxide of iron . . . . .	2·15
Oxide of copper . . . . .	trace
Oxide of manganese . . . . .	trace
Sulphuric acid . . . . .	6·48
Chlorine . . . . .	13·33
Carbonic acid . . . . .	10·04
Silica . . . . .	1·58
Charcoal . . . . .	11·78
	106·71

Omitting the charcoal and carbonic acid, and combining the chlorine as before, we have as follows:—

Potash . . . . .	36·23
Lime . . . . .	12·72
Magnesia . . . . .	11·14
Peroxide of iron . . . . .	2·62
Oxide of copper . . . . .	trace
Oxide of manganese . . . . .	trace
Chloride of potassium . . . . .	1·58
Chloride of sodium . . . . .	25·87
Sulphuric acid . . . . .	7·91
Silica . . . . .	1·93
	100·00

The molasses and sugar came from the same manufactory, and were made from the same sugar-cane.

LIII. *Letter from Professor LOOMIS of the New York University to Lieut.-Colonel SABINE, Foreign Secretary of the Royal Society, on the determination of differences of Longitude made in the United States by means of the Electric Telegraph, and on projected observations for investigating the Laws of the great North American Storms.*

DEAR SIR, New York University, Aug. 2, 1847.

I HAVE been for some time engaged upon a work in which you may perhaps feel some interest,—it is the exact determination of the difference of longitude between New York, Philadelphia and Washington, by means of the magnetic

telegraph. Morse's magnetic telegraph has been in operation between these places for a considerable time, and Prof. Bache proposed to use the line for the transmission of signals for the comparison of our local times for the use of the coast survey. Accordingly I erected a temporary observatory last season as near to this city as I conveniently could, and set up a transit instrument and clock. A wire was then carried from my observatory to the telegraph-office, thus connecting me with the regular Philadelphia line. A wire was also carried from the Philadelphia telegraph-office to the High School Observatory in Philadelphia, and another wire was carried from the Washington telegraph-office to the National Observatory. Thus three observatories, at New York, Philadelphia, and Washington, were in telegraphic communication; and having determined our local times by astronomical observations, we only needed some signal which could be heard simultaneously at the three places. This signal was afforded by the click of a magnet in the usual mode of telegraphic communication. Our plan of operation is as follows:—At ten in the evening, when the usual business of the telegraph company is concluded, our three observatories are put in communication with each other. After corresponding with each other long enough to ascertain that everything is in good order, New York commences giving clock signals. At the commencement of a minute by my clock I strike the key of my register, and a click is heard simultaneously at New York, Philadelphia, and Washington. The three observers record the time each by his own clock. At the expiration of 10<sup>s</sup> I give a similar signal, and all three record; after another 10<sup>s</sup> I do the same, and so on to twenty signals. Having waited one minute, Philadelphia repeats the same series of signals, and all record the time. We then wait another minute, and Washington repeats the same signals. Thus we have obtained sixty comparisons of our clocks, which will give our difference of longitude with as great accuracy as we can determine our local times.

In our first experiments we met with a great many disappointments, as might have been anticipated from the novelty and delicacy of the undertaking; but we have triumphed over them all. On five different nights we have transmitted good signals back and forth, and we propose to continue the comparisons until a further degree of accuracy is not to be expected. The errors of our clocks have not yet been rigorously computed, and we have not obtained final results; but we have made sufficient comparisons to know that the results of different nights agree remarkably well with each other. I

think the extreme discrepancy of different nights' work will amount to only a small fraction of a second. It appears to me that this mode of determining differences of longitude must supersede every other method between places which are connected by a telegraphic wire. The observations can be repeated indefinitely, and I think the longitude can be determined with a precision fully equal to that of the local times. I presume the same cannot be said of any other method yet practised. I have not heard of this method being tried in any part of Europe, though the application is very obvious. Can you inform me of any such trials?

In my former correspondence with you, and in my printed papers, I have more than once alluded to the importance of a combined movement in this country for meteorological observations. I am happy to say that the prospect of such a combination is brightening. You are probably aware that the Smithsonian Institution has been organized, and Prof. Joseph Henry has been placed at the head of it. The plan of organization is to appropriate £15,000 a-year to the promotion of *original researches*. Prof. Henry is disposed to include in this plan a grand meteorological campaign, to continue for three years,—to cover the entire area of the United States with the greatest possible number of observers: we want 300, and I think they could be obtained. I have been drawing up a paper for Prof. Henry which will be placed before the Smithsonian Institution, and also before Congress the coming winter. I think the plan will be carried into execution, *provided* we can obtain the co-operation of the British Government. You know from the papers which I have sent you that our great storms frequently extend far to the northward of the United States. When the centre of a storm travels along the valley of the St. Lawrence, its margin often extends to the Gulf of Mexico. Observations spread over the entire United States would frequently include only *half* the area of a violent winter storm; and this is the class of storms from which most is to be expected, because their phænomena are most strongly developed. Unless therefore we could obtain simultaneous observations from the British possessions on the north of us, we should feel that our observations were deprived of more than half their value. Will you not see if the British Government and the Hudson's Bay Company cannot be induced to co-operate with us? What I propose is, that at every government station a register should be kept for a period of one, two, or three years. I should hope 100 such stations could be procured. The first cost of the instruments would not be

great, and the expense of observing probably nothing at all. If your government will co-operate, I think the Smithsonian Institution will undertake the organization for the United States.

With much respect I remain,

Yours truly,

ELIAS LOOMIS.

LIV. *On the Algebraic Equation of the Fifth Degree.*

By the Rev. BRICE BRONWIN\*.

IT appears that the resolution of equations of the fifth and higher degrees into factors, one of which is of the second degree, depends upon the solution of the proposed equation itself. This circumstance appears to me deserving of notice, as it seems to indicate the impossibility of solving such equations in finite terms. Suppose

$$\left. \begin{aligned} x^5 + Ax^3 + Bx^2 + Cx + D &= (x^3 + ax^2 + bx + c) \\ (x^2 - ax + f) &= 0. \end{aligned} \right\} . \quad (1.)$$

Multiplying the two factors, and comparing the result with the first member, we find

$$b - a^2 + f = A, \quad c - ab + af = B, \quad bf - ac = C, \quad cf = D.$$

Eliminating  $b$  and  $c$  from these, we have

$$\begin{aligned} 2af^2 - (a^3 + Aa + B)f + D &= 0 \\ f^3 - (a^2 + A)f^2 + Cf + Da &= 0. \end{aligned}$$

From these we easily deduce

$$\begin{aligned} f^2 - (3a^2 + A)f + a^4 + Aa^2 + Ba + C &= 0 \\ (a^3 + Aa - B)f^2 - (2Ca - D)f - 2Da^2 &= 0. \end{aligned}$$

Eliminating  $f^2$  by  $2af^2 = (a^3 + Aa + B)f - D$ , we shall have two equations, in which  $f$  will be only of the first degree; and then, by eliminating it from these, there results an equation in  $a$  of the tenth degree; and it is obvious that  $f$ ,  $c$ , and  $b$  will be determined from  $a$  by simple equations.

Now let  $a_1, a_2, \&c.$  be the roots of the equation in  $a$ , and  $x_1, x_2, \&c.$  those of (1.); then, since  $x^2 - ax + f = 0$  must contain two of the last, we shall have

$$\left. \begin{aligned} a_1 &= x_1 + x_2, & a_2 &= x_1 + x_3, & a_3 &= x_1 + x_4, & a_4 &= x_1 + x_5, \\ a_5 &= x_2 + x_3, & a_6 &= x_2 + x_4, & a_7 &= x_2 + x_5, & a_8 &= x_3 + x_4, \\ a_9 &= x_3 + x_5, & a_{10} &= x_4 + x_5. \end{aligned} \right\} . \quad (2.)$$

\* Communicated by the Author.

To which we may add,

$$0 = x_1 + x_2 + x_3 + x_4 + x_5.$$

By eliminating  $x_1, x_2, \text{ &c.}$  from these, we find

$$3a_5 = -2a_4 - 2a_3 + a_2 + a_1, \quad 3a_6 = -2a_4 + a_3 - 2a_2 + a_1,$$

$$3a_7 = a_4 - 2a_3 - 2a_2 + a_1, \quad 3a_8 = -2a_4 + a_3 + a_2 - 2a_1,$$

$$3a_9 = a_4 - 2a_3 + a_2 - 2a_1, \quad 3a_{10} = a_4 + a_3 - 2a_2 - 2a_1,$$

which may be verified by putting for  $a_1, a_2, \text{ &c.}$  their values in  $x_1, x_2, \text{ &c.}$  Therefore six of the roots  $a_1, a_2, \text{ &c.}$  are linear functions of the remaining four, and the equation in  $a$  of the tenth degree is reducible to one of the fourth.

We also find

$$\left. \begin{aligned} x_1 &= \frac{1}{3}(a_1 + a_2 + a_3 + a_4), & x_2 &= \frac{1}{3}(2a_1 - a_2 - a_3 - a_4), \\ x_3 &= \frac{1}{3}(-a_1 + 2a_2 - a_3 - a_4), & x_4 &= \frac{1}{3}(-a_1 - a_2 + 2a_3 - a_4), \\ x_5 &= \frac{1}{3}(-a_1 - a_2 - a_3 + 2a_4). \end{aligned} \right\} (3.)$$

Now let the reduced equation in  $a$  be

$$a^4 + ma^3 + na^2 + pa + r = 0, \quad \dots \quad (4.)$$

the roots of which are  $a_1, a_2, a_3, a_4$ ; and therefore

$$-m = \Sigma(a_1), \quad n = \Sigma(a_1 a_2), \quad -p = \Sigma(a_1 a_2 a_3), \quad r = a_1 a_2 a_3 a_4.$$

Consequently,  $-m = 3x_1$  by (3.),

$$\begin{aligned} n &= 6x_1^2 + 2x_1(x_2 + x_3 + x_4 + x_5) + \Sigma(x_1 x_2) = 4x_1^2 + \Sigma(x_1 x_2) \\ &= \frac{4}{9}m^2 + A, \end{aligned}$$

because  $\Sigma(x_1) = 0$ ;

$$\begin{aligned} -p &= 4x_1^3 + 2x_1^2(x_2 + x_3 + x_4 + x_5) + x_1\Sigma(x_1 x_2) + \Sigma(x_1 x_2 x_3) \\ &= 2x_1^3 + x_1\Sigma(x_1 x_2) + \Sigma(x_1 x_2 x_3) = -\frac{2}{27}m^3 - \frac{1}{3}mA - B; \\ r &= x_1^4 + x_1^2\Sigma(x_1 x_2) + \Sigma(x_1 x_2 x_3 x_4) = \frac{1}{81}m^4 + \frac{1}{9}m^2A + C. \end{aligned}$$

Hence  $n, p$ , and  $r$  are given in terms of  $m$ , and  $m = -3x_1$  can only be found by solving (1.); or the resolution of the proposed into factors, one of which is of the second degree, depends upon the solution of the proposed itself.

We may introduce fifth roots if we please; thus, let

$$\lambda^4 + g\lambda^3 + h\lambda^2 + k\lambda + l = 0, \quad \dots \quad (5.)$$

the roots being

$$\lambda_1 = a_1^5, \lambda_2 = a_2^5, \lambda_3 = a_3^5, \lambda_4 = a_4^5.$$

Here we shall find, as before, putting for  $a_1, a_2, \&c.$  their values in  $x_1, x_2, \&c.$ , that

$$\begin{aligned} -g &= \Sigma(\lambda_1) = \Sigma(a_1^5) = 4x_1^5 + 5x_1^4(x_2 + x_3 + x_4 + x_5) \\ &\quad + 10x_1^3(x_2^2 + x_3^2 + x_4^2 + x_5^2) + 10x_1^2(x_2^3 + x_3^3 + x_4^3 + x_5^3) \\ &\quad + 5x_1(x_2^4 + x_3^4 + x_4^4 + x_5^4) + x_2^5 + x_3^5 + x_4^5 + x_5^5 = -27x_1^5 \\ &\quad + 10x_1^3\Sigma(x_i^2) + 10x_1^2\Sigma(x_i^3) + 5x_1\Sigma(x_i^4) + \Sigma(x_i^5). \end{aligned}$$

We may find  $h, k$ , and  $l$  in terms of  $g$ , as we found  $n, p$ , and  $r$  in terms of  $m$ ; and as  $\Sigma(x_1^2), \Sigma(x_1^3), \&c.$  are known functions of  $A, B, \&c.$ , we shall have  $g, h, \&c.$  functions of  $x_1$ . The determination of these therefore may be said to depend upon the solution of the given equation. If otherwise found, as they may be by finding the equation on which  $g$  depends, it must be by an equation of the fifth degree not reducible; for the five values of  $x_1, x_2, \&c.$  being distinct, there will be as many distinct values of  $g$ .

It may be observed that if we make  $\lambda$  any other integer function of  $a$ , not passing the fifth degree, we shall still have an ultimate equation to solve of the same degree.

To give two very simple examples of the equation in  $g$ , let

$$x^5 + Ax + B = 0.$$

Then

$$\Sigma(x_1^2) = 0, \Sigma(x_1^3) = 0, \Sigma(x_1^4) = -4A, \Sigma(x_1^5) = -5B;$$

and

$$g = 27x_1^5 + 20Ax_1 + 5B.$$

Eliminating  $x_1$  between this and  $x_1^5 + Ax_1 + B = 0$ , we have

$$(g + 22B)^5 + 7^4 A^5(g + 22B) - 7^5 A^5 B = 0.$$

Again, let  $x^5 + Ax^2 + B = 0$ . In this case

$$\Sigma(x_1^2) = 0, \Sigma(x_1^3) = -3A, \Sigma(x_1^4) = 0, \Sigma(x_1^5) = -5B;$$

and

$$g = 27x_1^5 + 30Ax_1^2 + 5B.$$

Eliminate  $x_1$  from this and  $x_1^5 + Ax_1^2 + B = 0$ , and there results

$$(g + 22B)^{\frac{5}{2}} + 3^{\frac{5}{2}} A^{\frac{5}{2}}(g + 22B) - 3^{\frac{5}{2}} A^{\frac{5}{2}} B = 0.$$

By making  $g + 22B = v$  in the first of these examples, and  $g + 22B = v^2$  in the second, the equations in  $v$  are similar to those in  $x$ , and are no way in a more solvable form.

Let us now take the equation of the sixth degree,

$$\begin{aligned} x^6 + Ax^4 + Bx^3 + Cx^2 + Dx + E &= (x^4 + ax^3 + bx^2 + cx + d) \\ (x^2 - ax + f) &= 0. \end{aligned}$$

There are fifteen ways in which this may be done, and consequently the equation in  $\alpha$  will be of the fifteenth degree. As before,

$a_1 = x_1 + x_2$ ,  $a_2 = x_1 + x_3$ ,  $a_3 = x_1 + x_4$ ,  $a_4 = x_1 + x_5$ ,  $a_5 = x_1 + x_6$ , &c., and

$$0 = x_1 + x_2 + x_3 + x_4 + x_5 + x_6.$$

If we eliminate  $x_1$ ,  $x_2$ , &c. from these sixteen equations, we shall have ten resulting equations between  $a_1$ ,  $a_2$ , &c., which will give  $a_6$ ,  $a_7$ , &c. in terms of the first five of these quantities. The equation of the fifteenth degree is therefore reducible to one of the fifth, or

$$a^5 + ma^4 + na^3 + pa^2 + qa + r = 0,$$

where

$$-m = a_1 + a_2 + a_3 + a_4 + a_5 = 4x_1.$$

The determination of  $m$  then will be the same thing as solving the given equation of the sixth degree. And it is easy to see that we shall arrive at results precisely the same in equations of a still higher degree.

If we resolve the given equation into the factors  $x^3 + ax^2 + bx + c$  and  $x^3 - ax^2 + fx + g$ , we shall have

$$a_1 = x_1 + x_2 + x_3, \quad a_2 = x_1 + x_2 + x_4, \quad \text{&c.},$$

and the equation in  $\alpha$  will be of the twentieth degree. But since  $\alpha_{11} = -\alpha_1$ ,  $\alpha_{12} = -\alpha_2$ , &c., the equation in  $\alpha^2$  will be only of the tenth degree. The reduced equation however, whether we find by it  $\alpha$  or  $\alpha^2$ , will be of a higher degree than the fifth.

Let us now return to (1.), or the equation of the fifth degree, in order to find Lagrange's final equation of the sixth degree.

Make

$$\begin{aligned} x_1 &= \theta^{\frac{1}{5}}_1 + \theta^{\frac{1}{5}}_2 + \theta^{\frac{1}{5}}_3 + \theta^{\frac{1}{5}}_4, & x_2 &= \alpha\theta^{\frac{1}{5}}_1 + \alpha^2\theta^{\frac{1}{5}}_2 + \alpha^3\theta^{\frac{1}{5}}_3 + \alpha^4\theta^{\frac{1}{5}}_4, \\ x_3 &= \beta\theta^{\frac{1}{5}}_1 + \beta^2\theta^{\frac{1}{5}}_2 + \beta^3\theta^{\frac{1}{5}}_3 + \beta^4\theta^{\frac{1}{5}}_4, & x_4 &= \gamma\theta^{\frac{1}{5}}_1 + \gamma^2\theta^{\frac{1}{5}}_2 + \gamma^3\theta^{\frac{1}{5}}_3 + \gamma^4\theta^{\frac{1}{5}}_4, \\ x_5 &= \delta\theta^{\frac{1}{5}}_1 + \delta^2\theta^{\frac{1}{5}}_2 + \delta^3\theta^{\frac{1}{5}}_3 + \delta^4\theta^{\frac{1}{5}}_4. \end{aligned}$$

Whence we find

$$\begin{aligned} 5\theta^{\frac{1}{5}}_1 &= x_1 + \alpha^4x_2 + \beta^4x_3 + \gamma^4x_4 + \delta^4x_5 \\ 5\theta^{\frac{1}{5}}_2 &= x_1 + \alpha^3x_2 + \beta^3x_3 + \gamma^3x_4 + \delta^3x_5 \\ 5\theta^{\frac{1}{5}}_3 &= x_1 + \alpha^2x_2 + \beta^2x_3 + \gamma^2x_4 + \delta^2x_5 \\ 5\theta^{\frac{1}{5}}_4 &= x_1 + \alpha x_2 + \beta x_3 + \gamma x_4 + \delta x_5, \end{aligned}$$

where  $1, \alpha, \beta, \gamma, \delta$  are the five roots of unity. If we make  $\beta = \alpha^2$ ,  $\gamma = \alpha^3$ ,  $\delta = \alpha^4$ , we have

$$\begin{aligned}5\theta^{\frac{1}{5}}_1 &= x_1 + \alpha^4 x_2 + \alpha^3 x_3 + \alpha^2 x_4 + \alpha x_5 \\5\theta^{\frac{1}{5}}_2 &= x_1 + \alpha^3 x_2 + \alpha x_3 + \alpha^4 x_4 + \alpha^2 x_5 \\5\theta^{\frac{1}{5}}_3 &= x_1 + \alpha^2 x_2 + \alpha^4 x_3 + \alpha x_4 + \alpha^3 x_5 \\5\theta^{\frac{1}{5}}_4 &= x_1 + \alpha x_2 + \alpha^2 x_3 + \alpha^3 x_4 + \alpha^4 x_5.\end{aligned}$$

Let  $\theta_1, \theta_2, \theta_3, \theta_4$  be the roots of

$$\theta^4 + M\theta^3 + N\theta^2 + P\theta + Q = 0.$$

Then

$$-M = \theta_1 + \theta_2 + \theta_3 + \theta_4;$$

to find which I employ

$$(u+v+w+z+t)^5 = \Sigma(u^5) + 5\Sigma(u^4v) + 10\Sigma(u^3v^2) + 20\Sigma(u^2vw) + 30\Sigma(u^2v^2w) + 60\Sigma(u^2vwz) + 120uvwzt,$$

collecting the terms separately, and reducing by means of

$$1 + \alpha + \alpha^2 + \alpha^3 + \alpha^4 = 0, \quad x_1 + x_2 + x_3 + x_4 + x_5 = 0,$$

$$x_2^2 + x_3^2 + x_4^2 + x_5^2 = \Sigma(x_1^2) - x_1^2, \quad x_1^3 + x_2^3 + x_3^3 + x_5^3 = \Sigma(x_1^3) - x_4^3, \text{ &c.};$$

and also

$$x_1^3 = x_1^2 x_1 = -x_1^2(x_2 + x_3 + x_4 + x_5),$$

$$\begin{aligned}x_1^3(x_2 x_5 + x_3 x_4) &= -x_1^2 x_2^2 x_5 - x_1^2 x_3^2 x_4 - x_1^2 x_4^2 x_3 - x_1^2 x_5^2 x_2 \\&\quad - x_1^3(x_2 x_3 x_4 + x_2 x_3 x_5 + x_2 x_4 x_5 + x_3 x_4 x_5), \text{ &c.}\end{aligned}$$

We thus find

$$\left. \begin{aligned}5^5(\theta_1 + \theta_2 + \theta_3 + \theta_4) &= 19\Sigma(x_1^5) - 10\Sigma(x_1^3)\Sigma(x_1^2) - 20\Sigma(x_1^3 x_2 x_3) \\&\quad - 130\Sigma(x_1^2 x_2^2 x_3) - 40\Sigma(x_1^2 x_2 x_3 x_4) + 480x_1 x_2 x_3 x_4 x_5 + 250 \\(x_1^2 x_2^2 x_4 + x_1^2 x_3^2 x_2 + x_1^2 x_4^2 x_5 + x_1^2 x_5^2 x_3 + x_2^2 x_3^2 x_5 + x_2^2 x_4^2 x_3 \\+ x_2^2 x_5^2 x_1 + x_3^2 x_4^2 x_1 + x_3^2 x_5^2 x_4 + x_4^2 x_5^2 x_2).\end{aligned} \right\} (6.)$$

The first six terms of the second member are all given, being symmetrical functions of  $x_1, x_2, \text{ &c.}$  Let their sum be  $R$ ; then, putting  $-M$  for  $\Sigma(\theta_1)$ , the above will be

$$-5^5 M - R = 250(x_1^2 x_2^2 x_4 + x_1^2 x_3^2 x_2 + \dots).$$

Or if we make

$$\frac{5^5 M + R}{250} = \varphi,$$

it will become

$$-\varphi = x_1^2 x_2^2 x_4 + x_1^2 x_3^2 x_2 + \dots$$

Now if we make  $x_1, x_2$  change places in the second member of the last, then  $x_1, x_3$ , and  $x_2, x_3$ , &c., we shall find that it has six different values, as stated by Lagrange. Thus

$$\begin{aligned}
 -\varphi_1 &= x_1^2 x_2^2 x_4 + x_1^2 x_3^2 x_2 + \dots \\
 -\varphi_2 &= x_1^2 x_2^2 x_4 + x_2^2 x_3^2 x_1 + \dots \\
 -\varphi_3 &= x_2^2 x_3^2 x_4 + x_1^2 x_3^2 x_2 + \dots \\
 -\varphi_4 &= x_2^2 x_4^2 x_1 + x_3^2 x_4^2 x_2 + \dots \\
 -\varphi_5 &= x_2^2 x_5^2 x_4 + x_3^2 x_5^2 x_2 + \dots \\
 -\varphi_6 &= x_1^2 x_5^2 x_4 + x_1^2 x_3^2 x_5 + \dots
 \end{aligned}$$

By adding these six equations, the sum of the second members will be a symmetrical function of  $x_1$ , &c., and we easily find  $-\Sigma(\varphi_1) = \Sigma(x_1^3 x_2^2)$ , a given quantity. Thus the coefficient of the second term of the equation of the sixth degree, of which the roots are  $\varphi_1$ ,  $\varphi_2$ , &c., is known, and the other coefficients may be found by means of it. It does not appear that there is any other relation between  $\varphi_1$ ,  $\varphi_2$ , &c.; and therefore it would seem that the equation of the sixth degree is not reducible. But if any one thinks that there may exist such a relation as

$$\varphi_1 = f(\varphi_2),$$

$f$  denoting a rational function, he may, from what precedes, make the trial. Success however seems so hopeless, that it is pity that time and talent should be wasted upon it.

Gunthwaite Hall, near Barnsley,  
October 2, 1847.

LV. *Letter from Capt. J. H. LEFROY, R.A., Director of the Magnetic Observatory of Toronto in Canada, to Lieut.-Colonel SABINE, R.A., on a great Magnetic Disturbance on the 24th of September 1847.*

Observatory, Toronto,  
September 24, 1847.

MY DEAR COLONEL,

THIS day has been distinguished by a greater disturbance than any we have had yet. The observed range of Declination was  $4^\circ 2'$ ; and I have little doubt that the actual range was greater, as the non-commissioned officer on duty, when he found that the movement was beyond the scale of the Observatory declinometer, lost time in sending for me, instead of at once lighting the lamp of the transportable one, and following it up on that. The observed range of horizontal force was over 600 divisions, or 0.052 of the horizontal force! The day has been raw and cloudy, with occasional rain, so that if an aurora existed, it could not have been seen. The disturbance seems to have begun between  $21^{\text{h}}$  and  $22^{\text{h}}$  Göttingen time on the 23rd, as the observation at  $22^{\text{h}}$  was decidedly unusual; but extra observations did not commence until  $23^{\text{h}} 20^{\text{m}}$ . The extreme disturbance began about  $0^{\text{h}} 35^{\text{m}}$  on the 24th, when both the large declinometer and large bifilar went off their scales.

At this time I was called, and we began to observe the trans-portable declinometer and bifilar. The last also went off the scale. The lowest reading of the former was 692·5 at 1<sup>h</sup> 0<sup>m</sup> Gött., and the highest 1126·0 at 1<sup>h</sup> 45<sup>m</sup>: this gives a range of 3° 36'·7; but at a subsequent period (5<sup>h</sup> 0<sup>m</sup> Gött.) a reading of 1177·2 was obtained, thus giving the enormous range of 4° 2'·3\*. I did not take a reading of your compass; but looking hastily at it, I perceived that during the great shock it was ranging more than 3° 20' from its usual position. As both bifilar scales were exceeded, we can only say that the range of that element between 0<sup>h</sup> and 1<sup>h</sup> Gött. exceeded 600 divisions, or 0·052 of its whole amount, on the testimony of two instruments; a fact which cannot, I think, but make it a most interesting question, what is the nature of a force subject to such immense variations, and how can they occur without affecting or being affected by the other physical agents in the globe? This disturbance was attended by a great degree of motion in the magnets, a peculiar mechanical agitation, which they only exhibit on rare occasions; it lasted, more or less, down to 12<sup>h</sup> Gött. As the results have not been made up, I cannot state precisely the range of inclination, but perhaps may do so before I close this.

After some little trouble, I think we have got Dr. Robinson's Anemometer into beautiful working order. If the principle on which the velocity is estimated is correct, as we must feel confident it must be, I think it has a great superiority over any other instrument of the kind yet invented. The facility and precision with which the velocity is measured, and the beautiful manner in which sudden changes are shown, together with the large scale on which directions are marked, make it a pleasure to use it, and make Osler's instrument look quite clumsy beside it; it is a most elegant instrument, and will give diurnal curves of velocity with a precision we have never attained before. I found on careful examination that Osler's anemometer, which has been up seven years, was much the worse for wear, and not in a condition to give a satisfactory comparison with the other; we have therefore, with a good deal of difficulty, taken it down. I have put it into the hands of an engineer here, and he is to refit all the essential parts, particularly the shoulder and collar of the vane, which were worn, and made the vane unsteady: we shall then be able to compare pressures and velocities.

Believe me, my dear Colonel,

Faithfully yours,

J. H. LEFRoy.

\* I think our greatest range before this was only 2° 23'; this occurred last April.

LVI. *On the Decomposition of Valerianic Acid by the Voltaic Current.* By H. KOLBE, Ph.D.\*

THE very remarkable changes which a series of organic compounds undergoes by means of the voltaic current, have induced me to make that mode of decomposition the subject of a thorough investigation. As however the numerous difficulties which present themselves in researches of this nature, and the immense extent of the field which opens before us, do not admit of the results being communicated in a complete and connected form, I beg to lay before the Chemical Society a short preliminary notice of the changes which valerianic acid undergoes when exposed to the oxidizing action of the voltaic current, reserving a more complete description of the products obtained till the investigation shall have been brought to a close.

When the voltaic current, excited by six pairs of Bunsen's carbo-zinc battery, is permitted to act on a concentrated neutral solution of valerianate of potash in the cold, two plates of platinum forming the electrodes, a brisk evolution of gas takes place simultaneously from both; the gases evolved consist of hydrogen, carbonic acid and a new carbo-hydrogen, but contain no traces of oxygen gas as long as the solution of valerianate of potash does not become too much exhausted. At the same time a light oily liquid separates at the surface, having an agreeable æthereal odour, and the alkaline solution ultimately consists chiefly of carbonate and bicarbonate of potash, the latter of which generally separates during the operation in a crystalline form.

The neutral æthereal oil is a mixture of two compounds; the one containing oxygen, the other perfectly free from it. By the action of an alcoholic solution of potash the former is decomposed, and the latter can then, by means of water, be separated unchanged. In the pure state it exists in the form of a light colourless æthereal oil, possessing an agreeable aromatic smell. It is insoluble in water, but soluble in alcohol and æther; it boils at 108° C. without decomposition, and has the composition  $C_8H_9$ . Oxygen and iodine are without action upon it, but chlorine, bromine, and fuming nitric acid form with it products of substitution.

The oil containing oxygen, which in the first instance was found mixed with this substance, I have not yet been able to obtain in a pure state; but several circumstances render it more than probable that it is formed by the union of valerianic acid with the oxide of the above carbo-hydrogen. An

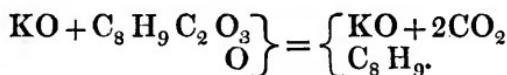
\* Communicated by the Chemical Society; having been read April 19, 1847.

alcoholic solution of potash treated with it is found to contain as a product of decomposition a considerable amount of valerianate of potash. But on account of the small quantity of material which has been at my disposal, I have not succeeded in separating the alcohol  $C_8 H_{10} O_2$ , which must have been formed at the same time.

The gaseous carbo-hydrogen, which is evolved with the hydrogen, is a substance analogous to olefiant gas ; it is characterized by a peculiar æthereal smell, and has a specific gravity double that of olefiant gas. It unites with chlorine even in the dark, forming a heavy oily liquid, having a marked similarity to chloreelayl, and is generally composed of a mixture of several products of substitution. Its rational composition is expressed by the formula  $C_8 H_8$ . The changes which valerianic acid undergoes, in accordance with the foregoing experiments, are capable of a very simple explanation, if we consider that acid as a conjugated combination of the carburetted hydrogen, or the radical  $C_8 H_9$  with oxalic acid, in a similar manner to the new view taken of the constitution of acetic acid. For whilst by the addition of one atom of oxygen oxalic acid becomes converted into carbonic acid, this radical is set free ; but a portion of it unites with the excess of oxygen to form an oxide, and this enters into combination with a portion of undecomposed valerianic acid, giving rise to a new æther,  $C_8 H_9 O + C_8 H_9 C_2 O_3$ .

Another portion of the radical is probably decomposed at the moment of its formation, in consequence of the concomitant evolution of heat into hydrogen and the gaseous carbo-hydrogen  $C_8 H_8$ . This latter view is supported by the fact, that if the temperature of the solution of valerianate of potash exceeds a certain point during the decomposition, not a single drop more of the ætherial oil is produced.

The following formula will throw light on this decomposition :—



Both butyric and acetic acids are acted on in a similar manner to valerianic acid ; the products of decomposition of acetic acid are all gaseous, and appear to contain oxide of methyle. Butyric acid gives in addition to the gaseous compounds a volatile oil composed of  $C_6 H_7$ .

The minute description of this product will form the subject of a future memoir.

The foregoing investigation has been carried out during the late session in the laboratory of Dr. Lyon Playfair, as whose assistant I have been engaged during that time ; and I

cannot allow this opportunity to pass by without thanking him for the kindness and liberality which he has shown in placing his laboratory at my disposal, in leaving so much of my time on my own hands, and in rendering me every assistance in his power.

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**LVII. An Account of Experiments with Galvanic Couples immersed in pure water and in oxygenated water. By Mr. RICHARD ADIE\*.**

**I**N the years 1845 and 1846, I published in the Edinburgh Philosophical Journal two series of experiments, made with a view to prove that the action of the water battery was maintained by absorbing oxygen from the atmosphere. Some of these experiments† show that it is the oxygen only that is drawn from the atmosphere, and that the presence of the other component parts is unnecessary. But there was one given to show that zinc and copper elements placed in a hermetically sealed tube along with pure water did not act, there being no flocculent deposit of oxide of zinc, which is formed in abundance when a minute aperture admits the atmosphere to the contents of the tube. After a lapse of two years, I examined an arrangement of this kind which had been hermetically sealed since December 1844; there was no apparent change, the water was transparent, and the metals bright. I had scarcely put the tube down when it burst with violence; this fact immediately satisfied me that the water battery must have a true decomposition of water action when it acts on zinc associated with copper or any other metal less oxidizable than the copper, independent of the much more extensive effect due to atmospheric oxygen. It is from a desire to trace by experiment the double action of this battery that I respectfully submit for the consideration of the Society the following results:—

In fig. 1, *a a a* represents six pieces of zinc soldered at *c c* to a corresponding number of pieces of copper *b b b*, arranged alternately as in the figure, and insulated from one another by strands of thread, *d d d d*. These were placed inside a flint-glass test-tube, which was after their insertion drawn off at the blowpipe to a capillary point. The tube was now filled with pure water, and to dislodge the air from among the fibres of the thread, the water was repeatedly boiled, closing and re-opening the capillary point at each boiling. When the air was well-removed, the tube was hermetically sealed,

\* Communicated by the Chemical Society; having been read April 19, 1847.

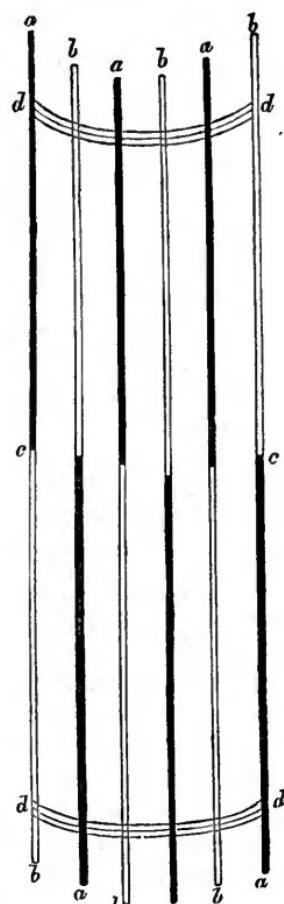
† Edinburgh New Phil. Journal, vol. xxxviii. p. 99, and vol. xl.

the water at the time of closing being near the boiling temperature. On cooling, the space left vacant by the contraction of the fluid was estimated to be  $\frac{1}{70}$ th of a cubic inch; the superficies of each plate  $\frac{1}{4}$ th of a superficial inch. From previous trials, I knew that when the above arrangement had a communication with the atmosphere, a flocculent deposit of the protoxide of zinc was soon perceived, which steadily increased. With the same hermetically sealed there was no such deposit; neither was there any perceptible change, until the bursting of the vessel after two years revealed another action of the battery. Judging from the thickness of the broken glass, I endeavoured at the time to make an approximate estimate of the volume of the gas generated, which in the vacant space of  $\frac{1}{70}$ th of a cubic inch, where it could lodge, produced pressure sufficient to burst the vessel: the result of my estimate gave less than a cubic inch of gas measured at the usual atmospheric pressure; for the development of which six zinc surfaces of  $\frac{1}{4}$ th of a superficial inch each had been two years in action. In a repetition of this experiment, with zinc filings in lieu of plates, a small quantity of gas was collected, and proved to be hydrogen.

Afterwards examining the inner surfaces of the fragments of the glass, the surface of the plates, and the fibres of the thread with a powerful lens, I found all of them covered with minute transparent crystals; the largest crop of these was on a copper surface opposite a spot on one of the zinc plates, to which nearly the whole of the corrosion of the metal appeared to have been confined. The red ground of the copper surface showed them most distinctly. On heating the copper the crystals parted with water of crystallization, and became circular white spots, very much resembling the protoxide of zinc.

My friend Mr. Waldie examined the thread; his process was, incinerating, dissolving the ash in hydrochloric acid, adding excess of potash, filtering to separate a trace of oxide

Fig. 1.



of iron, and treating the filtered liquid with hydrosulphuret of ammonia, which gave a yellowish white precipitate. This result proves that the minute transparent crystals among the fibres of the thread contained protoxide of zinc.

On a former occasion I employed either the air-pump or ebullition to deprive water used in exciting voltaic couples, of absorbed air. I gave preference to the method of boiling the water in the battery cell, as the more severe test, for showing how far a battery's action depended on oxygen from the atmosphere. The proof which appeared to me to furnish satisfactory evidence of the assistance given by absorbed oxygen, was when the indication in the galvanometer fell near to zero by prolonged boiling, and rose again when water holding dissolved air was thrown into the cell. According to this test, a zinc and platinum couple lose much of their action when excited by pure water boiled for near two hours. The galvanometer needles always indicated a slight action, however long the boiling was prolonged; but as I found when care was taken to have an atmosphere of steam resting on the surface of the boiling water the action of the couple was at its lowest, I was led to think that what remained might be due to oxygen from the atmosphere, which it was impossible to remove perfectly. The experiment given above renders this view no longer tenable; for if zinc and copper elements can at ordinary temperatures slowly generate gas, it must follow that all the elements less oxidizable than copper will at boiling temperatures possess, when associated with zinc, a voltaic action independent of oxygen from the atmosphere.

To try the effect of a zinc and copper couple excited by pure boiling water, I attached a pair of plates to a more sensitive galvanometer than I had hitherto used: the plates were placed in a Florence flask and covered to a depth of two inches with pure water previously distilled in glass vessels; there was only a small orifice in the cork at the top of the flask for a steam escape, in order to preserve the boiling surface from the atmosphere.

Previous to boiling, the galvanometer needle stood at  $50^{\circ}$   
Indication the moment boiling was about to begin .  $70^{\circ}$

... after long boiling . . . . .  $20^{\circ}$

A similar experiment with iron and copper elements:—

Indication previous to boiling . . . . .  $20^{\circ}$

... at boiling . . . . .  $46^{\circ}$

... after long boiling . . . . .  $7^{\circ}$

In this experiment the indication rose on cooling to  $30^{\circ}$ , and afterwards fell back.

When silver or platinum was substituted for the copper the

results were in the same order, giving the highest action at the time the water is parting with dissolved air, and lowest when the water is thoroughly boiled. Where zinc is the positive element the action falls considerably, as the boiled water cools before it has time to re-absorb air. With a little common salt added to the water of a zinc and platinum couple, ebullition serves greatly to exalt the action, for the arrangement is no longer dependent on oxygen from the atmosphere.

These experiments, in extension of those I formerly submitted to the public through the Edinburgh Philosophical Journal, do not militate against the general conclusion then drawn, that the water battery supported its action by absorbing oxygen from the atmosphere; they only show that there is in addition a minute degree of action when two metallic elements are excited by pure water.

Perhaps the experiments of the most importance for determining the theory of the action of gas absorbing galvanic couples, are those where one metal only is excited by oxygenated water; to illustrate this action I made the following experiments:—

Two slips of zinc cut side by side from the same sheet were placed in a running brook, the one opposed to a rapid part of the current, the other in a still place at the edge. Connecting these in the usual manner with the galvanometer, there was a permanent deflection of  $25^{\circ}$ ; and on changing the respective places of the plates in the stream without disturbing their attachments to the galvanometer, the needles immediately passed to the opposite side of the card; in both cases the piece of zinc in the current acted as a negative or platinode plate. With both plates in still water and a tube filled with oxygen inverted over one, the effect was the same. It is the greater supply of oxygen to the plate in the current which converts it into a negative or platinode. A cell containing two small silver wires and the cyanide of silver solution used for electro-plating was attached in place of the galvanometer, when, after a lapse of two hours, metallic silver was seen precipitated in a minute quantity on the silver wire connected with the piece of zinc in still water.

Two plates of iron were placed in the stream, under like conditions to the zinc; after two hours metallic silver was distinctly seen precipitated on the silver wire connected with the iron plate in still water.

The fact here shown, of two similar pieces of iron giving rise to a galvanic current capable of precipitating metallic silver, appears to me to be important, for it proves that the electricity in passing through the water intervening between

these two plates, either decomposes it with the aid of oxygen in solution, or that oxygenated water forms a binary compound, capable of acting as an electrolyte.

The fact of iron and oxygen uniting together at ordinary temperatures when moisture is present, is well known. It is the office performed by the water during this union, wherein lies the true ground of the theory of gas-absorbing batteries. A single plate of iron exposed to water and oxygen gas, has local differences on its surface which act in the same way as if the iron had been in two halves and placed in a stream in the manner described : the oxidation of the iron is developing a voltaic current which passes through the fluid from one point of the plate to another, either by a process of decomposition and re-composition of water, or by the decomposition of the compound formed by the solution of the gas in water.

The first of these views can only be supported by holding that the solution of oxygen so changes the affinities, that iron with its aid can at ordinary temperatures decompose water. I see no evidence sufficient to give probability to this hypothesis, while, if the second supposition be admitted to meet all the facts shown by experiment, it will establish the existence of an electrolyte more easily decomposed than water, and as universal in nature ; and account for the very reduced action of zinc and copper elements excited by pure water freed from absorbed air or from oxygen gas, the active principle derived from the air.

I may here take occasion to add, that a saturated solution of carbonate of potash and soda in an open cylindrical vessel has so shut out the oxygen of the atmosphere from some pieces of iron immersed in it, that now, after two years and four months immersion, there is no rust on the surface of the iron.

The experiments with two similar pieces of zinc or of iron placed in a running stream, as already described, were performed during the cold weather of winter, with the temperature varying from 32° F. to 42°. On the return of a little warmer weather I recommenced the experiments with iron plates, from a wish to try if two similar pieces of iron could be made to develope a voltaic current of the same electro-motive force as that derived from a platinum and iron couple excited by still water.

A piece of iron-wire was cut into two equal lengths ; each of those was bent into the form of a flat spiral (fig. 2), and a copper wire well-varnished was soldered to the iron at A, for connecting the plate with a small decomposing apparatus in the usual manner.

A pair of iron plates thus formed was taken to the banks of a small stream in Cheshire, called the Grange brook; one plate was placed in a current of moderate velocity, where the water poured through the interstices of the coils; the other plate was dropped into still water in a convenient place at the edge. In both plates the solderings at A projected above the surface and were kept dry.

When copper wire poles were placed in a decomposing cell filled with sulphate of copper solution, and connected with the galvanic couple formed of two pieces of iron (fig. 2), distinct evidence of the precipitation of metallic copper on the wire connected with the plate in still water, was observed after an hour's action, temperature  $45^{\circ}$ . One of the iron plates was now removed to a cell filled with water, and associated with a platinum plate, the arrangements for precipitating metallic copper remaining as before. With the temperature at  $42^{\circ}$ , the depositing of the metal did not proceed so actively as it had done with an iron plate in a current of water for a platinode.

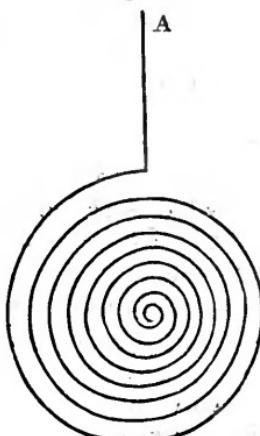
When the decomposing cell was filled with a solution of sulphate of zinc, and zinc wire poles supplied, after three hours' action, temperature  $46^{\circ}$ , the wire in connexion with the iron plate in still water showed, with the aid of a lens, a distinct deposit of metallic zinc. Repeating this experiment with an iron and platinum couple in still water, the metallic deposit of zinc was again obtained, temperature  $46^{\circ}$ , the rate of action in both experiments being, as near as I could judge, the same.

The inference from these results is, that a piece of bright iron placed in a current of water performs the office of a piece of platinum, as well as the latter metal does when excited by still water.

The quantities of metal precipitated during two or three hours' action of these oxygen absorbing batteries is in no case sufficient to give results by weight. I have tried experiments of one week each, but the changes in the level of the stream and other sources of derangement, made me prefer trials of two or three hours each, where there is no difficulty in detecting any decided change in the rate of action.

The Grange brook is supplied with water almost wholly by the drainage of a rather poor clay soil, reposing on the new red sandstone formation of the district.

Fig. 2.



The plate in the centre of the stream shows less rusting than the one at the edge in still water; but judging from the analogous case of the copper sheathing of a ship, it should waste away the fastest, the particles of peroxide of iron as they are formed being removed by the force of the stream, while the voltaic current developed during this action only circulates to some other point of the same plate, or belongs to what is called local action.

From the above results, the benefit to be obtained in a constant battery by making the negative plate rotate, should be apparent; but to prevent waste it would still be necessary to employ one of the more costly metals, which are not liable to oxidation.

In concluding these experiments, I may again notice, that a tube of oxygen suspended over a plate of iron in still water has the same effect as the current of the stream, converting the oxygenated plate into a platinode. The carbonic acid present in all surface water may by some be thought to perform an essential part in the ordinary rusting of iron. But where every care is taken to exclude this gas from a tube filled with oxygen, a small quantity of water, and a piece of iron, the oxidation of the iron proceeds with rapidity, accompanied by changes which appear to me to preclude the idea that even a trace of carbonic acid can be essential. The oxygen gas disappears; at first an abundant formation of red or peroxide of iron is seen; then, after the supply of oxygen has decreased, the green-coloured protoxide is gradually formed. These two oxides afterwards begin slowly to unite, and form the well-known black or magnetic oxide. In an experiment of this kind every trace of the red and green-coloured oxides had disappeared at the end of three months from the time of closing the tube, and there remained only an inky precipitate, which was proved to be the black oxide of iron.

**LVIII. On certain Improvements in the Construction and Supply of the Hydro-Oxygen Blowpipe, by which Platinum may be fused in the large way. By ROBERT HARE, M.D.\***

ON my return from Europe in 1836, I was very much in want of a piece of platinum of a certain weight, while many more scraps than were adequate to form such a piece were in my possession. This induced new efforts to extend the power of my blowpipe; and after many experiments, I succeeded so as to fuse twenty-eight ounces of platinum into one mass.

\* Communicated by the Author.

Although small lumps of platinum had been fused by many operators with the hydro-oxygen blowpipe as well as myself, it had not, up to the year 1837, been found sufficiently competent to enable artists to resort to this process. I am informed by Mr. Saxton, that some efforts which were made while he was in London were so little successful, that the project was abandoned. There was an impression that the metal was rendered less malleable when fused upon charcoal, as in the experiments alluded to. This is contradicted by my experiments, agreeably to which fused platinum is as malleable as the best specimens obtained by the Wollaston process, and is less liable to flake. Dr. Ure, on seeing specimens of platinum which I had elaborated and fused in the form of wire, of leaf, ingots and plate, said that there was no one in Europe who could fuse platinum in such masses. He also informed me that it had been found so difficult to weld platinum, that no resort was had to that process. In this I concur, having had the welding tried by a skilful smith, both with a forge heat, and with a heat given by the hydro-oxygen blowpipe. An incorporation of two ingots was effected on their being hammered together, when heated nearly to fusion; but on hammering the resulting mass cold, a separation took place along the joint by which the ingots were united.

The difficulty seems to arise from the rapidity with which the platinum becomes refrigerated. It seems to have a less capacity for heat than iron; and, not burning in the air as iron does, has not the benefit of the heat acquired by iron from its own combustion with atmospheric oxygen.

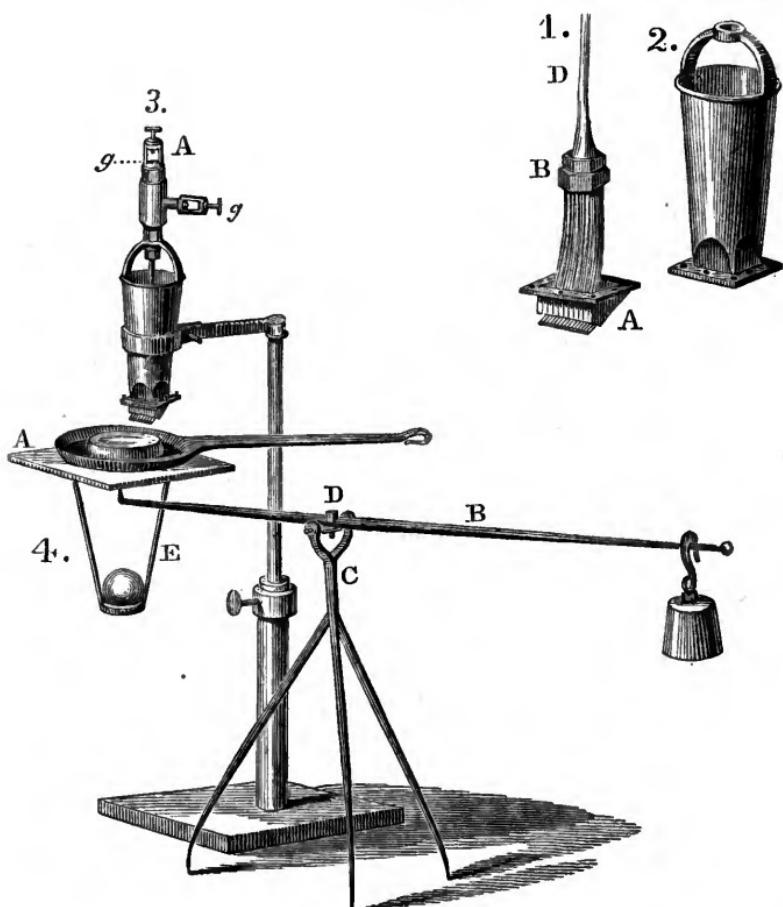
Lately, by means of the instrument and process which it is my object here to describe, I have been enabled to obtain malleable platinum directly from the ore, by the continued application of the flame. From some specimens of platinum I have procured as much as ninety per cent. of malleable metal. The malleability is not inferior to that of the best specimens obtained by reducing it to the state of sponge, through the agency of aqua regia and sal-ammoniac. There is however a greater liability to tarnish, arising probably from the presence of a minute portion of palladium.

Of the fusion of iridium and rhodium, I have already given an account in the Bulletin of the American Philosophical Society, which was subsequently embodied in an article in this Journal for August 1847.

It remains now to give an account of the apparatus employed in the fusion of platina on a large scale.

Fig. 1 represents the association of fifteen jet-pipes of platinum with one large pipe B D at their upper ends, so that

their bores communicate, by means of an appropriate brass casting, with that of the large pipe, the joints secured by hard solder. Their lower extremities are made to protrude about half an inch from a box A, of cast brass, their junctures, with the appropriate perforations severally made for them, being secured by silver solder. They come out obliquely in a line along one corner of the box, an interval of about a quarter of an inch alternating with each orifice. By means of flanges, the brass box is secured to a conical frustum of copper (fig. 2),



so as to form the bottom thereof, while the pipe, extending above the copper case, is screwed to a hollow cylinder of brass A, fig. 3, provided with two nozzles and gallows-screws *g g*, for the attachment of appropriate hollow knobs, to which pipes are soldered, proceeding from the reservoirs of oxygen and hydrogen. Cocks are interposed by which to regulate the emission of the gases in due proportion.

In connecting the pipes conveying the gases with the brass

cylinder A, fig. 3, care should be taken to attach that conveying oxygen to the upper nozzle, while the other, conveying hydrogen, should be attached to the lower nozzle; since by these means their great difference in density tends to promote admixture, which evidently it must be advantageous to effect.

The object of surrounding the jet-pipes with water by means of the copper box\*, is to secure them against being heated to such a degree as to cause the flame to retrocede and burn within them, so as finally to explode within the cylinder A, gg, fig. 3. It is preferable to add ice or snow to the water, in order to prevent undue heat.

Fig. 4 represents a moveable platform A, of cast iron, wholly supported upon the point of the iron lever D B, which is curved towards the extremity under the platform, so as to point upwards, and to enter a small central conical cavity made for its reception. The lever is supported by a universal joint upon the fulcrum C, so that by means of a sliding weight at one end, the platform and its appurtenances are counterpoised at the other. The platform is kept in a horizontal position by the cannon-ball, supported in a sort of iron stirrup terminating in a ring, in which the ball is placed. Upon the platform is situated an iron pan with a handle holding the brick, on a cavity in which, as already mentioned, the metal is supported. The apparatus being duly prepared and connected with the supply-pipes, the hydrogen is first allowed to escape and then the oxygen, until the ignition has attained apparently a maximum. The accomplishment of this object may of course require the adjustment of either cock several times, especially where there is any decline in the pressure either of the one or the other gas in its appropriate reservoir.

By means of the handles of the lever and of the pan, the operator is enabled to bring the metal into the position most favourable for the influence of the heat, while his hands and face are sufficiently remote to render the process supportable. In fusing any quantity, not being more than four ounces, the platform may be dispensed with, the handle of the pan being held in one hand of the operator, while by the other the cocks may be adjusted.

When the blowpipe of fifteen jets, or any larger, may be

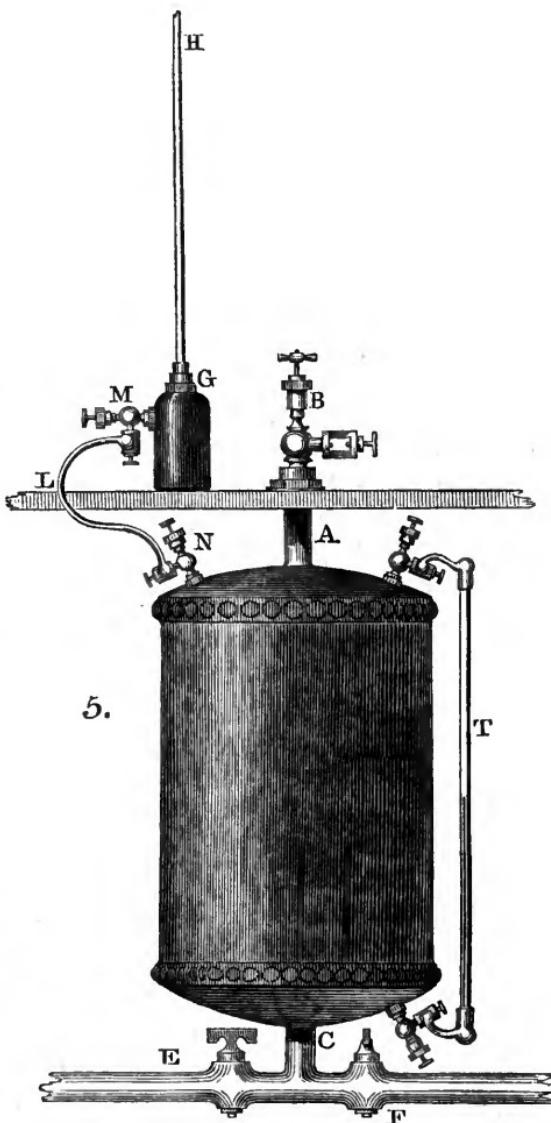
\* Since the engraving was made, I have preferred to use water-tight boxes, with gallows-screws and nozzles, situated one near the bottom on one side, the other on the opposite side near the top. By means of the lower nozzle, a pipe is attached, communicating with a head of cold water, the other being so situated as to carry the water into a waste pipe or large tub: a circulation may be kept up during the whole time that the operation is going on,

As a support, a brick kaolin is used, having an oblong ellipsoidal depression on the upper face for the reception of the metal to be fused.

employed, and the platform is necessarily resorted to, the cocks must be adjusted by an assistant.

Fig. 5 represents a cask made of boiler iron, three-sixteenths of an inch thick, so as to resist an enormous pressure. The joints are secured by riveting, as in constructing high pressure boilers.

This cask communicates with the hydrant pipes, so called, by which our city is supplied with water, of which the pressure varies from a half to more than two atmospheres, say from seven to thirty pounds per square inch, according to the number and bore of the cocks from which the water may be flowing at the time for the consumption of the community. Hence experiments, while using this head, are best



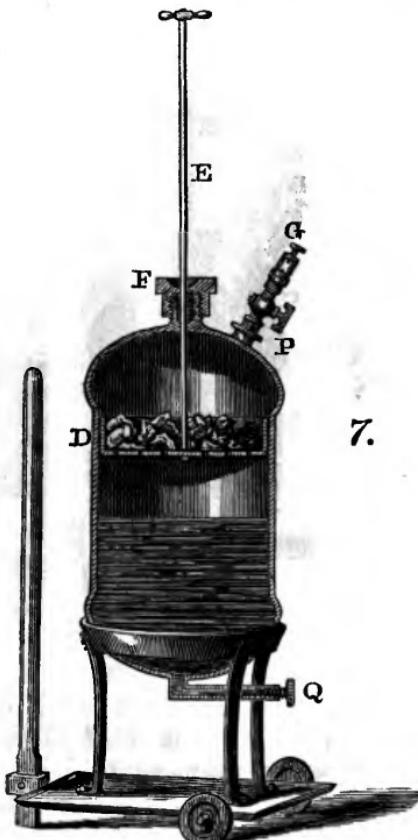
made towards bed-time, or between that time and sunrise. The vessel is filled with water by opening a cock F on one side of the pipe C, and allowing the air to escape through the valve-cock B. Being thus supplied, the cock F closed, and a communication with a bell-glass, into which oxygen is proceeding from a generating apparatus, being made by means of a flexible leaden tube, on opening the valve-cock B and the cock E, the water will run out and be replaced by gas from the bell. This process being continued till the iron cask is sufficiently supplied

with gas, the cock E must be shut. Whenever the gas is wanted for the supply of the blowpipe, it is only necessary to establish a communication between the valve-cock B and the upper gallows-screw (fig. 3) of the cylinder A, and to open the cock F, so as to admit the water to press upon the gas, the efflux being regulated by B, or preferable by a cock of the ordinary construction, one of which kind should be interposed at a convenient position between the valve-cock B and cylinder A.

T represents a glass tube, which, by due communication with the interior, shows the height of the water, and consequently the quantity of gas in the vessel.

G H represents a gauging apparatus, consisting of a cast-iron flask, of about a half pint in content, and a glass tube of about a quarter of an inch in bore, which should be at least five feet in height. The tube is secured air-tight into the neck of the flask, so as to reach nearly to the bottom within. The flask is nearly full of mercury. Under these circumstances, when a communication is made by a leaden pipe between the cavity of the flask and that of the reservoir, an equilibrium of pressure resulting, the extent of the pressure is indicated by the rise of the mercury in the tube.

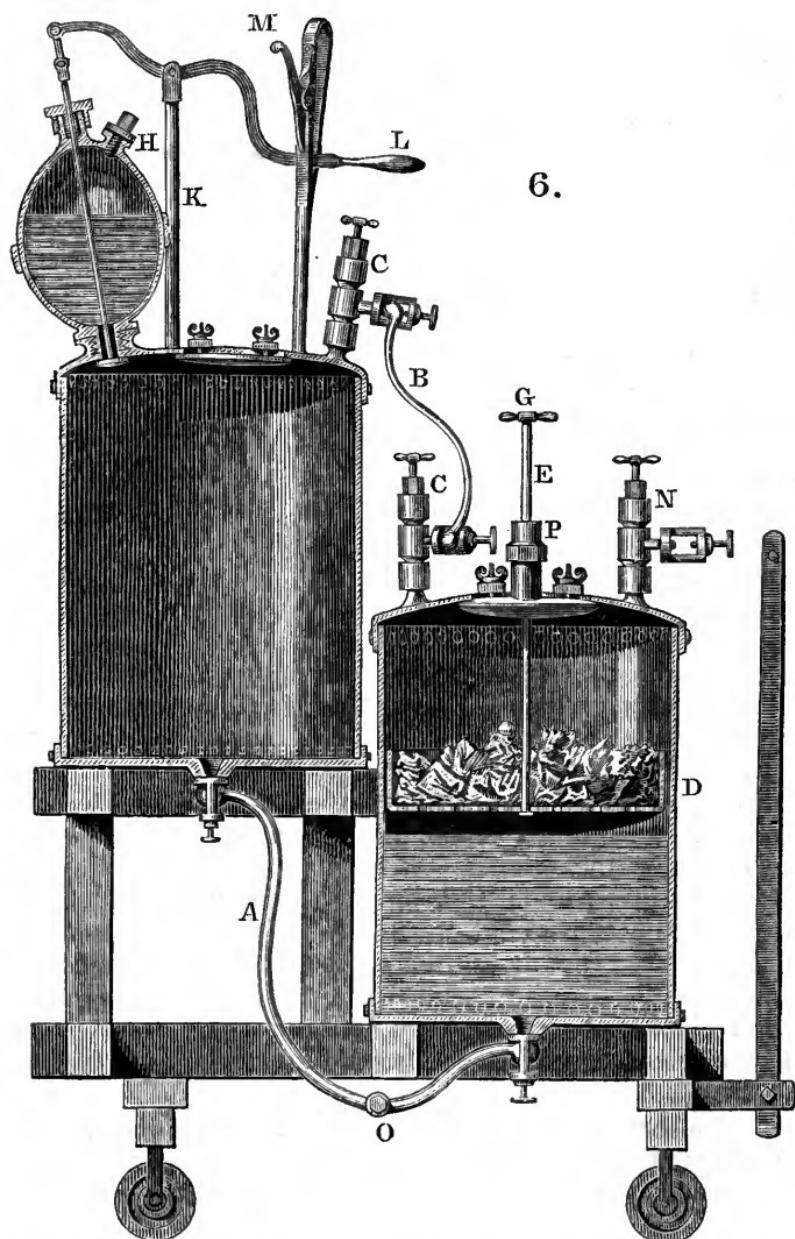
In order to generate hydrogen for the supply of a reservoir like that represented by the preceding figure, I have employed the vessel represented by fig. 7. This vessel, by means of a suitable aperture, susceptible of being closed by a screw-plug, is half-filled with diluted sulphuric acid. Being furnished with a tray D, punctured like a coal-sieve, and supported by a copper sliding-rod E, strips of zinc are introduced in quantity equal to the capacity of the tray. The sliding-rod passes through a stuffing-box F, at the top of the reservoir, so that the operator may, by lowering or raising



the tray, regulate or suspend the reaction between the zinc and its solvent, accordingly as the supply of hydrogen is to be produced, suspended, increased, or diminished.

The communication with the reservoir is open and regulated by means of a cock P, furnished with a gallows-screw G, for the attachment of a leaden pipe, as above described, in the process for supplying the reservoir with oxygen.

Another apparatus for producing a supply of hydrogen is represented in fig. 6. It consists of two similar vessels of



boiler iron, each capable of holding forty gallons. They are lined internally with copper, being situated upon a wooden frame, so that the bottom of one is two-thirds as high as the top of the other. The upper portions of these vessels communicate by a leaden pipe B, of about half an inch bore, furnished with a cock, while the lower portions communicate by another leaden pipe of a bore of one and a half inch.

The upper vessel is surmounted by a globular copper vessel, of about twelve inches in diameter, which, from its construction, renders it possible to introduce an additional supply of concentrated acid, while the apparatus is in operation, without reducing the pressure within the reservoir, by permitting the excess above the pressure of the atmosphere to escape. This object is accomplished as follows:—

The valve at the end of the rod attached to the lever L being kept shut by the catch M, the screw-plug H removed, the acid is introduced through the aperture thus opened. In the next place, the plug being replaced, and the valve depressed by means of the lever and rod, so as no longer to close the opening which it had occupied, the acid descends from the chamber into the cavity of the vessel beneath it. The valve is of course restored to its previous position as soon as the acid has effected its descent.

The lowermost vessel is furnished with a perforated copper tray, supported by a copper sliding rod, in a way quite analogous to that already described in the case of the copper reservoir. It is also supplied with zinc and its solvent in like manner, being made half-full of the diluted sulphuric acid. Of course, on contact being produced between the zinc and its solvent, the generation of hydrogen will take place. So long as the communication between the upper portions of the two vessels is open, the gas will extend itself into both, occupying the whole of the upper vessel, and that half of the lower one which is unoccupied by the liquid. But if in this way the pressure reaches to two atmospheres, as indicated by the gauge\*, on shutting the communication through the pipe B, the pressure in the inferior vessel will augment, that in the superior vessel remaining as before; but the liquid will consequently begin to pass out of the inferior vessel through the pipe A, and thus may lessen the contact between the acid and zinc, and finally suspend it altogether. Meanwhile the gas in the upper vessel being condensed to nearly half its previous bulk, the pressure will be nearly four atmospheres. It will,

\* I have used for a gauge an instrument like G, fig. 5, the tube being about two feet in length, and sealed at the upper end.

in fact, always be nearly double that which existed before the pipe B was closed.

In order that nearly the whole of the acid shall be expelled from the inferior vessel, the tray must be depressed till it touches the bottom of that vessel.

The pressure being four atmospheres at commencement, as soon as, by means of a pipe attached to the valve-cock N, an escape of gas is allowed, the acid is forced again upon the zinc, and thus prevents a decline of pressure to any extent sufficient to interfere with the process.

The gases may be used from a receiver in which they exist, in due proportion, safely by the following means :—

Two safety-tubes are to be made, not by Hemming's process exactly, but as follows :

A copper tube, silver soldered, of which the metal is about the eighth of an inch in thickness, is stuffed with the finest copper wire, great care being taken to have the filaments straight and parallel. The tube is then to be subjected to the wire-drawing apparatus, so as to compress the tube on its contents until the draught becomes so hard, as that it cannot be pushed further without annealing. The stuffed tube thus made is to be cut into segments, in lengths about equal to the diameter, by a fine saw. The surfaces of the sections are to be filed gently with a smooth file. By these means they appear to the naked eye like the superficies of a solid metallic cylinder. Brass caps being fitted on these sections, they are to be interposed by soldering, at the distance of a foot or more, into the pipe for supplying the jet. Under these circumstances, the posterior section becoming hot, may allow the flame to retrocede ; but the anterior section being beyond the reach of any possible combustion and remaining cold, will not allow of the retrocession ; and as soon as the flame passes the first section, the operator, being warned, will of course close the cock, and subject the posterior section to refrigeration before proceeding again.

But this plan of operating may be rendered still more secure by interposing a mercury bottle, or other suitable iron vessel, half-full of oil of turpentine, between the reservoir and safety tubes, as in the arrangement of a Woulfe's bottle. A leaden pipe proceeding from the reservoir is, by a gallows-screw, attached to an iron tube which descends into the bottle, so that its orifice may be near the bottom. The leaden pipe communicating through the safety tubes with the jet-pipe, is attached to the neck of the bottle. Thus the gaseous mixture has to bubble through the oil of turpentine in order to proceed through the safety tubes to the jet-pipe. If, while

this process is going on, the flame should, by retrocession, reach the cavity of the bottle, exploding in contact with the turpentine, a compound is formed, which is, *per se*, inexplosive from the excess of carbonaceous matter. Meanwhile the shock, acting on the surface of the oil, drives it into the bore of the iron tube, and thus, both by its chemical and mechanical influence, renders it utterly impossible that the flame should reach the cavity of the reservoir.

*Apparatus for the Fusion of Iridium or Rhodium or masses of Platinum less than five ounces in weight.*

For the fusion of either iridium or rhodium or masses of platinum not exceeding the weight of half an ounce, an instrument with three jets has been employed, the bore of each jet-pipe being such as not to admit a wire larger than the  $\frac{1}{32}$ nd of an inch in diameter. The flame produced by these means was quite sufficient to envelope the mass to which it was applied.

In fusing any lumps or congeries of platinum, not exceeding five ounces, an instrument has been used capable of giving seven jets of gas, issuing of course from as many pipes. Of these pipes, six protrude through the brass casting forming the bottom of the copper case constituting the refrigerator, so as to be equidistant from each other upon a circumference of three-fourths of an inch in diameter, the seventh protruding from the centre. The bores of these jets are such as not to admit a wire larger than  $\frac{1}{32}$ nd of an inch in thickness. Those of the larger instruments, represented by the accompanying engravings, were such as to admit wires of  $\frac{1}{24}$ th of an inch in thickness.

The jet-pipes may be made by the following process:—A thin strip of sheet metal, somewhat wider than the length of the circumference required in the proposed pipe, after being roughly turned about a wire so as to form an imperfect tube, is drawn through several suitable holes in a steel plate, as in the wire-drawer's process. Under this treatment the strip becomes converted into a hollow wire; the edges of the strip being brought into contact reciprocally, so as to leave only an almost imperceptible crevice. Having drawn one strip of platina in this way, another strip sufficiently wide nearly to inclose it is to be drawn over that first drawn, care being taken to have the crevices left at the meeting of the edges on contrary sides. The compound hollow wire or tube thus fabricated, is finally to be drawn upon a steel wire of the diameter of the requisite bore.

The following method of making jet-pipes, though more

difficult, is preferable, as there is less liability of the water of the refrigerator leaking into the bore.

Select a very sound and malleable cylinder of platina, of about three-eighths of an inch in thickness, perforate it by drilling in a lathe, so that the perforation may be concentric with the axis. A drill between one-sixteenth and one-eighth of an inch in diameter may be employed. In the next place, the cylinder may be elongated by the wire-drawing process until the proper reduction of metallic thickness is effected, the diameter of the bore being prevented from undergoing an undue diminution by the timely introduction of a steel wire.

Of course the metal must be annealed as often as it hardens, by drawing. For this purpose a much higher temperature is necessary in the case of platinum, than in that of either copper, silver, or gold.

The annealing is best performed by the hydro-oxygen flame. If charcoal be used, the greatest care must be taken to have the fireplace clean.

Agreeably to a trial made last spring, palladium may be used as a solder for platinum; and as it is nearly as difficult to fuse as this metal, it is of course for that purpose preferable to gold, where great heat is to be resisted. No doubt by employing palladium to solder the exterior juncture of the double drawn tubes above mentioned, they might answer as well nearly as when constructed of solid platinum.

This idea has been verified by a successful trial: and, moreover, silver has been successfully employed to solder the portions of the tubes, protected from heating by being within the cavity occupied by water. The portions which protrude beyond the brass box (see fig. 1) may be left unsoldered.

**LIX. On the Composition of the Bile of the Sheep. By J. W. GRIFFITH, M.D., F.L.S., Physician to the Finsbury Dispensary\*.**

**T**H E following analysis was made with the view of comparing the composition of this fluid with that of the biliary secretion in other animals; the conditions under which the analyses of the bile in them were performed have therefore been observed as closely as possible.

The bile in a perfectly fresh state was evaporated to dryness in a water-bath, the residue powdered and exhausted with alcohol of 840 specific gravity, the solution filtered, and the alcohol distilled off at 212° F.; the dry residue was next powdered, dissolved in absolute alcohol, the solution filtered

\* Communicated by the Author.

and digested with animal charcoal : when decolorized, it was again filtered, the alcohol distilled off, and the residue powdered, exhausted with æther, and perfectly dried at  $212^{\circ}$  F.

In this state it was almost white, having a slight tinge of buff.

The ash was prepared in a muffle at a low red heat.

I. 3.02 grains of the dried bile gave 0.305 ash = 10.09 per cent.; 4.83 gave 0.48 ash = 9.93 per cent.; 4.41, charred and washed in the manner proposed by Rose, gave 0.45 ash = 10.20 per cent.

The amount of chloride of sodium present in the prepared bile was very small; thus—

II. The 0.48 of ash from the 4.83 bile (I.) yielded 0.04 chloride of silver = 0.43 per cent. of chloride of sodium; 6.83 of the bile gave 0.05 chloride of silver = 0.38 per cent. of the chloride of sodium; the soda remaining, determined as sulphate, amounted to 0.99 = 6.32 per cent.

III. 4.045 bile burnt with chromate of lead, yielded 8.94 carbonic acid and 3.275 water, = carbon 60.07, and hydrogen 8.97 per cent.

IV. 4.005 bile gave 8.845 carbonic acid and 3.20 water, = carbon 60.22, and hydrogen 8.87 per cent.

V. 3.62 gave 2.29 ammonio-chloride of platinum = 3.97 nitrogen per cent.

Hence

	I.	II.
Carbon . . . . .	60.07	60.22
Hydrogen . . . . .	8.97	8.87
Nitrogen . . . . .	3.97	
Oxygen . . . . .	20.29	
Soda . . . . .	6.32	
Chloride of sodium . . .	0.38	0.43
	<hr/>	
	100.00	

In all the specimens of the ash of bile which I have examined, on solution in water and the addition of nitrate of silver, the yellow colour resulting from the formation of the tribasic phosphate of silver was distinctly perceptible in admixture with the white colour of the chloride. The yellow precipitate was dissolved by a drop of nitric acid. Whether the phosphate thus indicated arises from the solubility of the phosphate of soda existing in the bile prior to the separation of the mucus in an alcoholic solution of bile, or to the oxidation by the heat of a certain amount of phosphorus existing in the electro-negative constituent of this fluid, and its subsequent combination with the soda, I have not determined.

By comparing the above results with those obtained by Kemp, Theyer and Schlosser, &c., from the analysis of the bile of the ox, the two fluids are seen to exhibit the same composition.

The nature of the true constitution of the bile is still a matter of doubt; the opinion that it was a compound of an electro-negative substance (bilic acid) with the base soda seemed latterly to have been almost established. If however the experiments of Mulder, which have recently been published, should be confirmed, no dependence can be placed upon direct analysis, since from the moment of the secretion of that fluid it begins to undergo decomposition: even on drying at  $212^{\circ}$  F. ammonia is evolved, and the bile ceases to be perfectly soluble in water; and all fresh bile contains ammonia. Should these results be proved correct, the analysis of this fluid must be conducted in a different way from that which has been ordinarily adopted. On dissolving some purified fresh sheep's bile in alcohol, adding a drop of muriatic acid, then a little chloride of platinum, and setting the mixture aside, I obtained a precipitate of the ammonio-chloride, the crystals of which were perfectly distinct under the microscope. This appears to give support to Mulder's statement that ammonia is present in the bile.

9 St. John's Square, August 1847.

## LX. *Notice respecting the Meteor of September 25, 1846.*

*By the Rev. J. SLATTER.*

*To the Editors of the Philosophical Magazine and Journal.*

Rose Hill, near Oxford,

GENTLEMEN,

October 23, 1847.

**A**S I do not generally see your Publication, I was quite unaware of any accurate notice having been put on record of a large meteor which appeared one night in the end of September 1846. During the late meeting of the British Association at Oxford, a conversation arose, from which I learnt that Sir John Lubbock had observed it also, and made a communication to your Magazine respecting it\*.

I saw it myself in lat.  $51^{\circ} 43' 50''$  N., and long.  $1^{\circ} 13' 45''$  W. It passed from E. to N.E. at an altitude at first of about  $50^{\circ}$ , declining somewhat towards the end of its course, but not more to my notion than would be caused by perspective, supposing its path to have been on a meridian line, and parallel to a tangent at the earth's surface. The night was very cloudy, but there were many openings between the clouds. The body

\* In the January Number for this year, p. 4.

of the meteor was visible at these points, and appeared round, and certainly not less than  $15'$  in diameter,—I should say double that measure. I was in some degree enabled to judge by estimating, after it had passed, the size of the gaps in the clouds where it was fully visible. The light was very great, enabling me to see surrounding objects as plainly as during a vivid flash of lightning, and lasted about two seconds.

Now to compare my observation with the diagram and notice sent you last year by Sir J. Lubbock, I conclude he must have seen the meteor just before its disappearance; in which case, the course being very much foreshortened, it would occupy the portion of the heavens which he has indicated by a blurred mark of his pencil. On this hypothesis it must have passed about  $8^\circ$  or  $10^\circ$  from the zenith of his place of observation, which I suppose to be in longitude  $0^\circ 4'5$  W., lat.  $51^\circ 20'$  N.

I consider then that the meteor at the end of the phænomenon bore N. by  $10^\circ$  W. at Sir J. Lubbock's station at an altitude of about  $40^\circ$ ; at my station at the same instant it bore N.E. at an altitude of  $45^\circ$ . From these data, I calculate its height to have been sixty-one miles nearly.

But taking its course as upon a meridian line, and the estimated altitude when due east of me, I make its height about fifty-six miles. Considering the roughness of the data, I regard this degree of accordance, proceeding upon two independent methods, as tolerably satisfactory. Then, if my estimate be at all correct, it had a diameter of at least 700 yards, and its velocity was thirty-six miles in a second.

I remain, Gentlemen,

Your obedient servant,

JOHN SLATTER.

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LXI. *On the Aurora Borealis, as it was seen on Sunday evening, October 24, 1847, at Blackheath. By JAMES GLAISHER, Esq., of the Royal Observatory, Greenwich.*

THIS day having been remarkable for one of the most brilliant displays of Aurora Borealis which it has ever been my good fortune to witness, it has occurred to me that a notice of its principal phases, so far as they fell under my own observation, may not be unacceptable to your readers.

The barometer reading during the day previous had declined rapidly, and during this day it had increased as rapidly. The day had been for the most part overcast, and light rain had fallen occasionally; towards evening the sky became per-

fectly cloudless; the night was beautiful, and the full moon shone with unusual brilliancy.

At about 6<sup>h</sup> 30<sup>m</sup> P.M. a bright red streamer was seen to spring up from the N.W.

At 6<sup>h</sup> 40<sup>m</sup> another streamer was seen in the N.W., and at the same instant one sprung up from the N.; both of which were of a beautiful red.

At 6<sup>h</sup> 56<sup>m</sup> a less brilliant streamer was seen in the N.W., and within three minutes after this time, several faint streamers were seen in the N., N.N.W. and N.W.

From 7<sup>h</sup> to 7<sup>h</sup> 12<sup>m</sup> a few streamers were seen, and after this time no trace of the Aurora could be seen for some time.

Between 7<sup>h</sup> 30<sup>m</sup> and 9<sup>h</sup> 40<sup>m</sup> there were occasional streamers, both white and red, appearing between the N.W. and the E.N.E.

At 9<sup>h</sup> 55<sup>m</sup> a splendid column of red light appeared in the N.W., whose base was about 5° in breadth. This pyramid exhibited all the tints of the most brilliant sunset, and appeared to be composed of streamers whose colours shaded from the most intense crimson into the ruddiest and most brilliant orange, which orange parts again contrasted with the ruddy hue of the next portion, forming by means of contrast upon contrast an endless gradation of shade and colour,—a truly sublime and gorgeous appearance. About this time, the furnace glow which pervaded this appearance increased in intensity, and had all the appearance of the reflexion from an immense conflagration; in the mean time the orange colour entirely disappeared, and gave place to an uniform deep crimson, increasing, as before stated, in intensity, and apparently in denseness.

At 10<sup>h</sup> 0<sup>m</sup> the same appearance continued as above; but in addition to it, there was a collection of vertical columns of light from 2° to 3° in breadth; and from the E.N.E. there was a column similar in form and colour to the one in the N.W., with the exception of being less brilliant. These two red columns formed the east and west boundaries of the fan-like appearance of the whole mass, all the columns of which converged to a point a few degrees S. of the zenith.

The columnar appearances situated between the red columns were of the most silvery light, shaded with a most delicate and pure gray; they were perpetually glancing and shifting upwards and downwards; the lower parts of each column would suddenly glance into the place of the upper portion of the same column, whilst the upper portion would shoot higher towards the zenith, and then both together suddenly descend. This vibrating motion was simultaneous in all the columns, excepting the splendid

red portions at either termination, which remained immovable, though it rather appeared, that as the central silvery light fluctuated, now bright, now dim, these rosy extremities fluctuated in direct opposition, their rosy hue becoming fainter and inclining to a neutral tint in proportion to the increase of the silvery brightness. The whole variation of appearance somewhat resembled the reflexion cast upon a wall by a Gothic casement lighted from within by some fitful and inconstant light. Towards 10<sup>h</sup> 12<sup>m</sup> a considerable diminution in the brilliancy of the light, fleecy, silvery columus took place; the regular and casement-like appearance disappeared by degrees and assumed more of the character of the extremities, although they still continued their fitful, glancing and radiating motion. During these appearances two or three milk-white, cloud-like masses came up from the N.W. and slowly moved towards the S.E.; each of these masses seemed to have a kind of pulsation within themselves.

At 10<sup>h</sup> 19<sup>m</sup> little could be seen of the Aurora, excepting the red column in the N.W.; this still retained much brilliancy, though all else seemed merged into the sky, when at times, like the bursting of a firework, a stream would spring up from this column, white and brilliant, except at their upper portions, which were tinged with rose colour.

About this time, the moon, which had been shining upon a cloudless sky, was suddenly surrounded with a splendid corona, exhibiting concentric circles, first of a neutral tint, next of violet, then green, and the outermost red; the external boundary of the latter passed nearly midway between the moon and the planet Mars; this appearance continued at its extreme brilliancy a short time only, but more dimly it continued for a long time.

From 10<sup>h</sup> 30<sup>m</sup> to 11<sup>h</sup> 0<sup>m</sup>, with the exception of an occasional streamer, there was no appearance of the Aurora; and at times no aurora at all was visible.

At 11<sup>h</sup> 14<sup>m</sup>, to this time no arch-formation had been seen, or bank of vapour; a bright arch however was supposed to have formed at about this time, but, if so, it continued a short time only.

Shortly after 11<sup>h</sup> 15<sup>m</sup> a faint stream or column of white light was seen in the N.N.E., and a splendid red patch of light, nearly in the east, was seen, which grew very bright, and the phænomenon at midnight exhibited an appearance as beautiful as any of those that had preceded it. An arch appeared extending from the N.W. to the S.E.; from this arch very bright and flickering pencils of light darted out, both upwards and downwards.

At 12<sup>h</sup> 30<sup>m</sup> the streams were frequent; the arch now extended from the N. by W. to the E. by N., and at every part of this arch an occasional streamer, with its taper-like form, sprung up; and this appearance continued till after 13<sup>h</sup>.

I did not observe any halo around the moon at any time, and the Aurora, with the exception of the beautiful white clouds, was confined to the northern hemisphere.

On Friday the 22nd, and on Saturday the 23rd, the magnetic instruments at the Royal Observatory were greatly disturbed, as they were during the auroral appearances on the 24th ultimo\*.

Many of the preceding observations were made by an assistant at my residence, as my own attention was almost completely occupied by observations of the magnetical instruments; so much so, that I was obliged to neglect some of its finest appearances, but which I believe were pretty well observed as above described. The watch by which the times were taken was compared at about midnight, so that the several times are true Greenwich mean solar times.

JAMES GLAISHER.

Blackheath, Oct. 26, 1847.

P.S. An Engraving of its appearance, as seen at about 10<sup>h</sup>, will appear in the Illustrated London News of Oct. 31.

## LXII. *Proceedings of Learned Societies.*

### ROYAL SOCIETY.

[Continued from p. 227.]

June 17, "ON the Solution of Linear Differential Equations." By 1847. Charles James Hargreave, Esq., B.L., F.R.S., Professor of Jurisprudence in University College, London.

1. By the aid of two simple theorems expressing the laws under which the operations of differentiation combine with operations denoted by factors, functions of the independent variable, the author arrives at a principle extensively applicable to the solution of equations, which may be stated as follows:—"if any linear equation  $\phi(x,D).u=X$  have for its solution  $u=\psi(x,D).X$ , this solution being so written that the operations included under the function  $\psi$  are not performed or suppressed, then  $\phi(D,-x).u=X$  has for its solution  $u=\psi(D,-x).X$ ." The solution thus obtained may not be, and often is not, interpretable, at least in finite terms; but if by any transformation a meaning can be attached to this form, it will be found to represent a true result.

An important solution immediately deducible from this principle is given by Mr. Boole in the Philosophical Magazine for February

\* See the weekly reports of the weather supplied by the Astronomer Royal to the Registrar-General.

1847, and is extensively employed in the present paper. It is immediately obtained by making the conversion above proposed in the general equation of the first order and its solution.

2. By the use of this theorem and the general theorems above referred to, the solution of the equation

$$D^2u + 2Q.Du + \left( c^2 + Q^2 + Q' - \frac{m(m+1)}{x^2} \right) u = P,$$

is found in the form

$$u = x^m e^{-\int Q dx} (D^2 + c^2)^{m-1} \left\{ x^{-1} (D^2 + c^2)^{-m} (x^{-(m-1)} \cdot e^{\int Q dx} \cdot P) \right\};$$

of which various particular cases and transformations are given and discussed; including the well-known forms

$$D^2u + \frac{2m}{x} Du \pm c^2 \cdot u = P,$$

$$D^2u + bDu + \left( c^2 - \frac{m(m-1)}{x^2} \right) u = P,$$

$$\frac{d^2u}{dz^2} + \left( \frac{c}{2n-1} \right)^2 z^{-\frac{4n}{2n-1}} \cdot u = 0,$$

and extensions of these forms.

The application of the process to equations of the third and higher orders gives rise to solutions of analogous forms; and in particular the equation

$$(a_n x + b_n) D^n u + \dots + (a_1 x + b_1) Du + (a_0 x + b_0) u = X$$

is solved in the form

$$u = (a_n D_n + \dots + a_1 D + a_0)_{-1} \varepsilon^{\frac{b_n}{a_n} D} (D - \alpha)^A (D - \beta)^B \dots \left( x^{-1} \left\{ \varepsilon^{-\frac{b_n}{a_n} D} (D - \alpha)^{-A} (D - \beta)^{-B} \dots X \right\} \right),$$

$$\text{where } \frac{b_n z^n + b_{n-1} z^{n-1} + \dots}{a_n z^n + a_{n-1} z^{n-1} + \dots} = \frac{b_n}{a_n} + \frac{A}{x - \alpha} + \frac{B}{x - \beta} + \dots;$$

and by the application of the theorems first referred to, a still more general form is solved.

The solutions above-mentioned are subject to the important restriction that  $m$ ,  $A$ ,  $B$ , &c. (denoting the number of times that the operations are to be repeated) must be integer; but in the subsequent part of the paper, a mode is suggested of instantaneously converting these solutions into definite integrals not affected by the restriction.

3. The interchange of symbols above suggested frequently renders available forms of solution which otherwise would not be interpretable in finite terms. The operation  $(\phi D)^m$  is not intelligible if  $m$  be a fraction; but if by any legitimate process this be changed into the factor  $(\phi(-x))^m$ , the restriction ceases to operate. By the ap-

plication of this principle, solutions of a simple character are obtained for ( $b$  being integer),

$$(x^2 + c^2)D^2u - 2axDu + b(2a - b + 1)u = P,$$

$$\frac{d^2u}{dt^2} - \frac{b(b+1)}{\cos^2 t}u = P,$$

$$\frac{d^2u}{dt^2} - b(b+2)\frac{1}{(1-t^2)^2}u = P,$$

$$\varphi x \cdot D^2u + \psi x \cdot Du + (\psi' x - \varphi'' x)u = P.$$

4. The advantages of the forms above given in this particular, that the number and order of the operations in the solution are expressed *generally*, and not by a series of substitutions involving changes of the variable as in the ordinary mode of solving Riccati's equation, appear more clearly in the application to partial linear differential equations. Thus, the equation

$$\frac{d^2u}{dx^2} + \frac{2n}{x} \frac{d^2u}{dxdy} + \left(\frac{n^2}{x^2} - k^2\right) \frac{d^2u}{dy^2} - \frac{n}{x^2} \frac{du}{dy} - \frac{m(m-1)}{x^2} \cdot u = \psi(x, y),$$

which may be solved by  $m$  successive substitutions, receives its solution in the general form

$$u = x^m \varepsilon^{-n \log x} \cdot D' (D^2 - k^2 D'^2)^{m-1} \\ \left\{ x^{-1} (D^2 - k^2 D'^2)^{-m} \{ x^{-(m-1)} \varepsilon^{n \log x D'} \psi(x, y) \} \right\};$$

which exhibits at a glance all the successive processes to be performed upon  $\psi(x, y)$  in order to arrive at the result. It will be observed that the process  $\varepsilon^{\varphi x} \cdot D'$  performed upon  $\psi y$  denotes  $\psi(y + \varphi x)$ . Among other results worthy of notice on this branch of the subject may be noticed the solution of

$$\frac{d^2u}{dpdq} + \frac{a}{p+q} \left( \frac{du}{dp} + \frac{du}{dq} \right) + \frac{a(a-1) - m(m-1)}{(p+q)^2} = \varphi(p, q)$$

(solved by Euler in a series when there is no second term); viz.

$$u = x^{m-a} (D^2 - D'^2)^{m-1} \left\{ x^{-1} (D^2 - D'^2)^{-m} \{ x^{a-m+1} \cdot \psi(x, y) \} \right\};$$

$\psi$  being determined from  $\varphi$  by the equations  $\frac{p}{q} = x \pm y$ ; and the solution of

$$(a_n x + b_n) \frac{d^n u}{dx^n} + (a_{n-1} x + b_{n-1}) \frac{d^n u}{dx^{n-1} dy} + \dots + (a_0 x + b_0) \frac{d^n u}{dy^n} = \varphi(x, y)$$

which is readily deduced from the solution of the corresponding form in ordinary equations.

5. The character of most of the solutions may be described as follows: they consist in the performance (repeated  $m$  times) of ope-

rations of the form  $\phi D$  upon the second side  $X$ ; multiplication by the factor  $x^{-1}$ ; and the performance (repeated  $m-1$  times) of the inverse operation  $(\phi D)^{-1}$ ; and it will be seen that, in all cases where  $X=0$ , it is sufficient to perform the direct operation  $\phi D$  a single time.

It is a remarkable phenomenon connected with the solutions last mentioned, that they are instantaneously convertible into definite integrals by changing  $\phi D$  into  $\phi z$ , multiplying by  $\varepsilon^{zx}$ , changing  $x^{-1}$  into  $D'^{-1}$  ( $D'$  denoting differentiation with regard to  $z$ ), and assigning proper limits for the integral. In this manner definite integrals are immediately found for

$$D^2u + 2Q \cdot Du + \left( Q^2 + Q' - c^2 - \frac{m(m-1)}{x^2} \right) u = 0,$$

$$D^n u + \frac{u}{x} = 0,$$

$$D^n u + x \cdot u = 0,$$

$$(a_n x + b_n) D^n u + \dots + (a_0 x + b_0) u = 0,$$

and other forms.

6. The application of the principle above stated to equations of finite differences gives solutions for the equations

$$(a_n x + b_n) u_{x+n} + \dots + (a_1 x + b_1) u_{x+1} + (a_0 x + b_0) u_x = Q_x,$$

$$(a_n x + b_n) \Delta^n u_x + \dots + (a_1 x + b_1) \Delta u_x + (a_0 x + b_0) u_x = Q_x;$$

and where the number of operations to be performed is denoted by a fraction, solutions are found in the form of definite integrals.

The solution of the first when  $Q_x=0$  is

$$\begin{aligned} u_x &= c_1 \int_0^\alpha (a_n v^n + \dots + a_1 v + a_0)^{-1} v^{b_0} (v-\alpha)^{A_1} (v-\beta)^{A_2} \dots v^{x-1} dv \\ &\quad + c_2 \int_0^\beta (a_n v^n + \dots + a_1 v + a_0)^{-1} v^{b_0} (v-\alpha)^{A_1} (v-\beta)^{A_2} \dots v^{x-1} dv \\ &\quad + \&c.; \end{aligned}$$

and that of the second is somewhat similar.

From some investigations effected by interchanging the symbols  $x$  and  $D$  in the solution of the general linear equation in finite differences of the first order, it would seem that definite summations may be used to represent the solutions of certain forms of equations. Thus a partial solution of

$$\varepsilon^{-x} \cdot u - D^n u = c$$

is  $c \Sigma (\Gamma z)^n \varepsilon^{zx}$  from  $z = -\infty$  to  $z = 0$ .

7. In attempting the solution of some equations by means of successive operations, not consisting exclusively of  $D$  combined with

constants, but involving also functions of  $x$ , the only result which appeared to the author worthy of notice is the solution of

$$D^2u + bDu + c^2u - n(n+1)\frac{u}{\cos^2 x} = X;$$

from a particular case of which, the general solution of Laplace's equation,

$$\frac{d}{d\mu}\left((1-\mu^2)\frac{du}{d\mu}\right) + \frac{1}{1-\mu^2}\frac{d^2u}{dy^2} + n(n+1).u = 0,$$

may be found in the simple form

$$u = \varepsilon^{\tan^{-1}(\mu\sqrt{-1})}\frac{d}{dy}\left(\frac{d}{d\mu}\right)^n \left\{ (1-\mu^2)^n \varphi(y - 2\tan^{-1}(\mu\sqrt{-1})) \right\},$$

with a similar function using  $-\sqrt{-1}$  for  $\sqrt{-1}$ .

#### CAMBRIDGE PHILOSOPHICAL SOCIETY.

[Continued from p. 311.]

On the Symbolical Equation of Vibratory Motion of an Elastic Medium, whether Crystallized or Uncrystallized. By the Rev. M. O'Brien, late Fellow of Caius College, Professor of Natural Philosophy and Astronomy in King's College, London.

The object of the author in this paper is twofold: *first*, to show that the equations of vibratory motion of a crystallized or uncrystallized medium may be obtained in their most general form, and very simply, without making any assumption as to the nature of the molecular forces; and *secondly*, to exemplify the use of the symbolical method and notation explained in two papers read before the Society during the present academical year.

First, with regard to the method of obtaining the equations of vibratory motion.

This method consists in representing the *disarrangement* (or state of relative displacement) of the medium in the vicinity of the point  $xyz$  by the equation

$$\delta v = \frac{dv}{dx} \delta x + \frac{dv}{dy} \delta y + \frac{dv}{dz} \delta z + \frac{1}{2} \frac{d^2v}{dx^2} \delta x^2 + \frac{d^2v}{dxdy} \delta x \delta y + \text{&c.} - \text{&c.}$$

(where  $v = \xi\alpha + \eta\beta + \zeta\gamma$ ,  $\xi\eta\zeta$  denoting, as usual, the displacements at the point  $xyz$ , and  $\alpha\beta\gamma$  being the *direction units* of the three coordinate axes), and in finding the *whole* force brought into play at the point  $xyz$  (in consequence of this disarrangement) by the *symbolical addition* of the different forces brought into play by the several terms of  $\delta v$ , *each considered separately*. It is easy to see that these different forces may be found with great facility, without assuming anything respecting the constitution of the medium more than this, that it possesses *direct* and *lateral elasticity*. By *direct elasticity* we mean that elasticity in virtue of which *direct* or *normal* vibrations

take place ; and by *lateral*, that in virtue of which *lateral* or *transverse* vibrations take place.

The forces due to the several terms of  $\delta v$  are obtained by means of the following simple considerations.

Let AB be any line in a perfectly uniform medium, and conceive the medium to be divided into elementary slices by planes perpendicular to AB ; let OM( $=x$ ) be the distance of any slice PP' from any particular point O of AB, and suppose this slice to suffer a displacement equal to  $\frac{1}{2} cx^2$  ( $c$  being a constant) in the direction OAB,

and the other slices to be similarly displaced. Then it is evident that the medium suffers by these displacements a uniformly increasing *expansion* in the direction OB, and a uniformly increasing condensation in the direction OA ; the rate of increase both of the expansion and condensation being  $c$ . Now in all known substances, whether solid, fluid, or gaseous, a disarrangement of this kind would bring into play on the slice O a force along the line AB proportional to the rate of increase  $c$ , i. e. a force  $Ac$ , A being a constant depending upon what we may call the *direct elasticity* of the substance.

Again, suppose that the slice PP' receives a displacement  $\frac{1}{2} cx^2$

in the direction OC perpendicular to AB, and the other slices similar displacements. Then the line AB will become curved into a parabola A'OB', and all the lines of the medium parallel to AB will be similarly curved, the radius of curvature being equal to  $\frac{1}{c}$  and per-

pendicular to AB. Now in all known substances\* a disarrangement of this kind would bring into play upon the slice O a force in the direction OC proportional to the curvature  $c$ , i. e. a force  $Bc$  depending upon what we may call the *lateral elasticity* of the substance.

Lastly, suppose that MP $=y$ , and that the point P of the medium receives a displacement  $cxy$  parallel to AB, and the other points similar displacements. Then the slice PP' will, in consequence of this kind of displacement, turn through an angle  $\tan^{-1}(cx)$  into the dotted position, and the other slices will suffer similar rotations, those on the other side of O, such as QQ', turning the opposite way. Now it is easy to see that a disarrangement of this kind produces a uniformly increasing expansion in the direction OC, and a uniformly increasing condensation in the direction OC', the rate of increase both of the expansion and condensation being  $c$ . But the expansion and condensation here described are quite different from that previously noticed ; since it is produced, not by displacements parallel to C'C, but by *lateral* displacements, i. e. *perpendicular* to C'C. On this account all that we can assert without further investigation is, that the force brought into play upon an element at O by this disarrangement acts along the line C'C, and is proportional to  $c$ , i. e. equal to  $Cc$ , where C is some constant evidently depending in some way both upon the *direct* and *lateral* elasticity of the medium.

\* Fluids and gases possess lateral elasticity as well as solids, only in a comparatively feeble degree.

There is however a very simple way of finding the precise value of the force brought into play by a disarrangement of this kind; for if we turn the axes of  $x$  and  $y$  in the plane of the paper through an angle of  $45^\circ$ , it appears that this disarrangement is nothing but a combination of the two kinds of disarrangement previously noticed; and from this it immediately follows, in the case of an uncrystallized medium, that the force brought into play at O is  $(A-B)c$ ; in other words, the coefficient C, which must be multiplied into  $c$ , in order to give the force brought into play by the disarrangement  $cxy$ , is equal to the coefficient of direct elasticity (A) minus the coefficient of lateral elasticity (B).

In the case of a crystallized medium, it may be shown that *six relations*, corresponding to the relation  $C=A-B$ , are most probably true, and are *essential* to Fresnel's theory of transverse vibrations; that is to say, the medium is capable of propagating waves of transverse vibrations if these six conditions hold, but otherwise it is not.

In employing the above considerations to determine the equations of vibratory motion, the directions AB and C'C are always taken so as to coincide with some two of the three coordinate axes; and it is this circumstance that makes the method peculiarly applicable to crystallized media. Indeed, if it were necessary to take the lines AB and C'C in any directions but those of the axes of symmetry, the above considerations would not apply without considerable modification.

The equations of vibratory motion obtained by this method for an uncrystallized medium, are the well-known equations involving the two constants A and B. The equations obtained for a crystallized medium are perfectly free from any restriction of any kind, are applicable to all kinds of substance, whether we suppose its structure to be analogous to that of a solid fluid or gas, and hold for all kinds of disarrangement, whether consisting of normal or transverse displacements, or both.

When we introduce the six relations between the constants above alluded to, and moreover assume that the vibrations constituting a polarized ray are *in* the plane of polarization, we arrive at Professor MacCullagh's equations\*. If, on the contrary, we suppose the vibrations to be *perpendicular* to the plane of polarization, we arrive at equations which agree exactly with Fresnel's theory in every particular†.

If we introduce these six relations into the equations for crystallized media deduced from M. Cauchy's hypothesis, that the molecular forces act along the lines joining the different particles of the medium, it will be found that these equations are immediately reduced to the equations for an uncrystallized medium. From this it follows that M. Cauchy's hypothesis cannot be applied to any but uncrystallized media. In fact, it may be easily proved that if the

\* Given in a paper read to the Royal Irish Academy, Dec. 9, 1839, page 14.

† On this subject see a paper by the late Mr. Greene in the seventh volume of the Cambridge Transactions, p. 121.

equations derived from this hypothesis be true, a crystallized medium is incapable of propagating transverse vibrations.

*Secondly, respecting the use of the symbolical method and notation above alluded to.*

The application of the symbolical method and notation to the subject of vibratory motion is very remarkable, and leads to equations of great simplicity. In the case of an uncrystallized medium, the three ordinary equations of motion are included in the single symbolical equation

$$\frac{d^2v}{dt^2} = B \left\{ \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \right\} v + (A - B) \left( \alpha \frac{d}{dx} + \beta \frac{d}{dy} + \gamma \frac{d}{dz} \right) \left( \frac{d\xi}{dx} + \frac{d\eta}{dy} + \frac{d\zeta}{dz} \right).$$

If we employ the notation  $\Delta u'.u$ , and assume the symbol  $\mathfrak{D}$  to represent the operation

$$\alpha \frac{d}{dx} + \beta \frac{d}{dy} + \gamma \frac{d}{dz},$$

the equation of motion becomes

$$\frac{d^2v}{dt^2} = B(\Delta \mathfrak{D} \cdot \mathfrak{D})v + (A - B) + \Delta \mathfrak{D} \cdot v;$$

or, by using the notation  $Du'.u$  also, it may be put in the form

$$\frac{d^2v}{dt^2} = \{ A \mathfrak{D} \Delta \mathfrak{D} \cdot - B (\mathfrak{D} \mathfrak{D} \cdot)^2 \} v.$$

The symbol  $\mathfrak{D}$  written before any quantity  $U$  which is a function of  $xyz$ , has a very remarkable signification; the *direction unit* of the symbol  $\mathfrak{D}U$  is that direction *perpendicular* to which there is no variation of  $U$  at the point  $xyz$ , and the *numerical magnitude* of  $\mathfrak{D}U$  is the *rate of variation* of  $U$ , when we pass from point to point in that direction.

The symbols  $\Delta \mathfrak{D} \cdot v$  and  $\mathfrak{D} \mathfrak{D} \cdot v$  have also remarkable significations.  $\Delta \mathfrak{D} \cdot v$  is a numerical quantity representing the *degree of expansion*, or what is called the *rarefaction* of the medium at the point  $xyz$ .  $\mathfrak{D} \mathfrak{D} \cdot v$  represents, in magnitude, the degree of *lateral disarrangement* of the medium at the point  $xyz$ , and, in direction, the *axis about which* that displacement takes place.

These two symbols may be found separately by the integration of an equation of the form

$$\frac{d^2U}{dt^2} = C \left( \frac{d^2U}{dx^2} + \frac{d^2U}{dy^2} + \frac{d^2U}{dz^2} \right).$$

When the six conditions above alluded to are introduced, the equation of motion for a crystallized medium becomes

$$\begin{aligned} \frac{d^2v}{dt^2} = & \left( A_1 \alpha \frac{d}{dx} + A_2 \beta \frac{d}{dy} + A_3 \gamma \frac{d}{dz} \right) \Delta \mathfrak{D} \cdot v \\ & + \mathfrak{D} \mathfrak{D} \cdot \left\{ \left( B_2 \frac{d\eta}{dz} - B'_1 \frac{d\xi}{dy} \right) \alpha + \left( B_3 \frac{d\xi}{dx} - B'_1 \frac{d\xi}{dz} \right) \beta + \right. \\ & \left. \left( B_1 \frac{d\xi}{dy} - B'_2 \frac{d\eta}{dx} \right) \gamma \right\}, \end{aligned}$$

where  $A_1 A_2 A_3$  are the three coefficients of *direct* elasticity with reference to the three axes of symmetry, and  $B_1 B'_1 B_2 B'_2 B_3 B'_3$  the six coefficients of *lateral* elasticity with reference to the same axes.

If the vibrations be transverse, this equation is reducible to the form

$$\frac{d^2v}{dt^2} = -(D\mathbb{D}.)^2(a^2\xi\alpha + b^2\eta\beta + c^2\zeta\gamma) \\ = -(D\mathbb{D}.)^2(a^2\alpha\Delta\alpha + b^2\beta\Delta\beta + c^2\gamma\Delta\gamma)v,$$

assuming the vibrations of a polarized ray to be *perpendicular* to the plane of polarization.

The well-known condition that a plane polarized ray may be transmissible without subdivision, and the velocity of propagation may be immediately deduced from this equation.

If we assume the vibrations of a polarized ray to be *in* the plane of polarization, the equation becomes

$$\frac{d^2v}{dt^2} = -D\mathbb{D}.(a^2\alpha\Delta\alpha + b^2\beta\Delta\beta + c^2\gamma\Delta\gamma)D\mathbb{D}.v.$$

This includes Professor MacCullagh's three equations.

#### ROYAL ASTRONOMICAL SOCIETY.

[Continued from p. 146.]

May 14, 1847.—Extract of a letter from Mr. Adams, with new Elements of Neptune.

"The following elements of Neptune have been obtained by taking into account Prof. Challis's observations made since the reappearance. \* \* \* The elements are now sufficiently correct to enable me to approximate to the perturbations of Neptune by the action of Uranus, in order to compare more accurately the ancient observations of 1795 with those . . . made recently. I have used the old observations, supposing the elements not to have changed. I hope immediately to set about a new solution of the perturbations of Uranus, starting with a very approximate value of the mean distance. \* \* \* I do not think, with Professor Pierce, that the near commensurability of the mean motions will interfere seriously with the results obtained by the treatment of perturbations; but it will be interesting to see how nearly the real elements can be obtained by means of the perturbations."

#### *Elements of the Orbit of Neptune.*

Mean longitude, Jan. 1, 1847, G. M. T...	328 13 54·5	M. Eq. 1847·0
Longitude of perihelion (on the orbit)...	11 13 41·5	
Longitude of ascending node .....	130 5 39·0	
Inclination to ecliptic .....	1 47 1·5	
Mean daily motion .....	21·3774	
Semi-axis major.....	30·2026	
Eccentricity of orbit .....	0·0083835	

On the communication of Mr. Adams's paper, the Astronomer

Royal gave orally a continuation of the history of Neptune, embracing the principal points that have been ascertained since his communication of Nov. 14, 1846. The planet having been actually discovered in the heavens by means of certain predicted elements, the fair presumption was that those elements were very approximately correct. Adopting these elements, therefore, Mr. Hind examined Lalande's and other observations, with the hope of finding some former observation of the planet as a star now missing, but satisfied himself that there was none. In the meantime, the continuation of the observations of the planet in the last months of 1846, and the comparison of them with Professor Challis's early observations of August, led to some unexpected conclusions. It was found that, though one *place* of the planet might be very well represented by M. Le Verrier's or Mr. Adams's elements, yet the apparent *movement* of the planet could not be represented within several minutes. Elements were then investigated from the observations themselves (without any reference to the preceding deductions from the perturbations of Uranus) by Mr. Adams in England (see Monthly Notices for March, p. 244), and by Professor Pierce and Mr. Sears C. Walker in America. Attention is particularly due to the former of these investigations, in which are exhibited, not only the results for the different elements, but also for the probable error of each. The most important conclusion was, that the planet certainly moved in a much smaller orbit, and probably in an orbit of much smaller eccentricity, than that indicated by the calculations of perturbation. With elements thus roughly corrected, the orbit was again traced back through the ancient observations; and it was found by Dr. Petersen of Altona, and Mr. Sears C. Walker, that a star observed by Lalande on May 10, 1795, and now missing from the heavens, was very probably the planet. The observation however was marked doubtful in Lalande's printed volume: and to this circumstance is probably due a most remarkable discovery. The manuscripts of Lalande's observations were some years ago transferred by his representatives to the observatory of Paris. To examine into the presumption of doubt in the observation, the astronomers of the Observatory of Paris referred to the originals, and there they found that the observation of May 10, 1795, was entered without any expression of doubt at the time; that an observation of May 8, 1795, was omitted in the printed volume; that it was omitted solely because it could not be reconciled with the observation of May 10; and that, upon reducing both properly, they exhibit most distinctly the retrograde motion of a planet nearly parallel to the plane of the ecliptic, the right ascension and the polar distance having both changed in the proper proportion. It seems now inconceivable to us that an astronomer, having his attention strongly called to the difference between the two days' results, should rather assume that there were in the observations two independent errors (one of right ascension and one of polar distance), than that the body observed was really a planet. With the place of the planet at an epoch so distant, its elements are ascertained with great accuracy.

It is remarkable that the missing star, to which allusion has been made, is actually entered as an observed star in the Berlin Star-Map; and this circumstance prevented Mr. Adams from tracing the new orbit of the planet so soon as he would otherwise have done. This insertion of an unobserved star can be accounted for only on the supposition that the star had been taken by the observer in his working-catalogue as a zero-star, and had then been inserted as a matter of course.

The mean distance of Neptune from the sun now appears, instead of 38, to be something near 30; and its periodic time, instead of 220 years, to be nearly 166. It is certainly a most curious thing (in which much is owing to chance) that elements, now known to be extremely erroneous, should have accounted for the perturbations of Uranus through 150 years with such accuracy, and should also have given the planet's place, *for the particular year in which the attention of astronomers was first strongly directed to it*, with such precision. It remains to be seen whether the new elements of Neptune will, with any possible mass, explain the perturbations of Uranus. In any case, Bode's law, on the assumption of which the original investigations of M. Le Verrier and Mr. Adams entirely depended, fails completely.

*Calcul détaillé d'une Inégalité Nouvelle à Longue Période, qui existe dans la Longitude moyenne de la Lune.* By M. Hansen.

The author states that he has lately made known to some astronomers a discovery of two inequalities in the motion of the moon, whose periods are respectively nearly 273 and 239 years. Denoting by  $g$ ,  $g'$ ,  $g''$  the geocentric mean anomaly of the moon, and the heliocentric mean anomalies of the earth and Venus, these inequalities are—

$$27''\cdot4 \times \sin(-g - 16g' + 18g'' + 35^\circ 20'\cdot2) \\ + 23''\cdot2 \times \sin(8g'' - 13g' + 315^\circ 30') ;$$

of which the first depends on a new argument, while the second depends on the argument of an equation of long period in the motion of the earth, discovered by Mr. Airy.

As the calculation of those parts of the coefficients which depend on the product of the square and cube of the sun's disturbing force by the disturbing force of Venus is extremely laborious, and is moreover connected with other unpublished calculations of other inequalities of the moon, it does not appear possible to publish it at present. Indeed M. Hansen does not consider himself able yet to answer for their perfect correctness, though he has the strongest reason to believe that they are very nearly correct. The present paper therefore includes only the calculation of that part of the coefficient of the first inequality which depends on the first power of the disturbing force.

It appears difficult to abstract very completely the remainder of this paper, but the following indications will enable a person acquainted with the developments of physical astronomy to follow the whole process.

The perturbing function  $\Omega$  for the moon as disturbed by Venus being formed, it will be found that it may be expanded in a rapidly

converging series of fractions, whose numerators contain successive powers of  $r$ , the moon's radius vector, and whose denominators contain different powers of the same multinomial (which, when eccentricities and inclinations are omitted, is a trinomial) that occurs in computing the perturbations of the earth by Venus. Upon expanding any of these fractions with trinomial denominator, there occur terms depending on  $16g'' - 16g'$ ,  $17g'' - 17g'$ , and  $18g'' - 18g'$ : then, upon introducing the inclinations and eccentricities, the first (among other combinations) will be multiplied by  $\sin^2 \frac{1}{2} \text{ inclin.} \times \cos 2g'' - 2\nu$  (where  $\nu$  is the difference of longitude of node and perihelion of Venus), and also (in other terms) by  $e''^2 \cos 2g''$ ; the second by  $e''.e' \cos g'' + g'$ ; and the third by  $e'^2 \cdot \cos 2g'$ . Each of these combinations produces terms whose argument is  $18g'' - 16g'$ . Then upon multiplying these terms by a power of  $r$ , since the expression for any power of  $r$  contains  $e \cdot \cos g$ , the product will contain terms depending on  $18g'' - 16g' - g$ . The coefficient necessarily contains one of the following products of three small quantities:  $e \cdot \sin^2 \frac{1}{2} \text{ inclin.}, e \cdot e''^2, e \cdot e'' \cdot e', e \cdot e'^2$  (of which the first is the most important), and it is therefore extremely small; but the resulting perturbation is made important by the excessive smallness of the divisor introduced in integration. It is well known that the divisor in this case will be proportional to  $\left( 18 \frac{dg''}{dt} - 16 \frac{dg'}{dt} - \frac{dg}{dt} \right)^2$ ; and, taking for  $\frac{dg''}{dt}$ , &c., the value in sexagesimal seconds corresponding to a Julian year.

$$\frac{dg''}{dt} = 2106641'' \cdot 3$$

$$\frac{dg'}{dt} = 1295977'' \cdot 4$$

$$\frac{dg}{dt} = 17179157'' \cdot 4$$

$$\text{whence } 18 \frac{dg''}{dt} - 16 \frac{dg'}{dt} - \frac{dg}{dt} = 4747'' \cdot 7,$$

a quantity very small in comparison with  $\frac{dg}{dt}$ .

In this manner the greatest part of the term in question is produced. Other parts arise from the circumstance that, the dimensions of the moon's orbit being slightly altered, the perturbing force of the sun upon the moon is not the same as it would otherwise be.

M. Hansen remarks that this term is remarkable as depending upon higher multiples of the anomalies than have ever before been considered, and as having the longest period in proportion to the periodic time of the disturbed body that is yet known.

The term depending on  $8g'' - 13g'$  arises mainly from the circumstance, that, the earth's motion in its orbit being different from what it would have been without the perturbation by Venus, the disturbing force of the sun upon the moon is not the same as if that perturbation had not existed.

M. Hansen states that he has examined several inequalities of long period in the moon's motion which hitherto have escaped notice, but that in no other instance does the coefficient amount to 1".

In concluding the account of this remarkable discovery, it is gratifying to add that it explains almost precisely the observed inequality in the moon's mean motion, which for the last fifty years has troubled physical astronomers.

After the reading by the Secretary of a portion of this paper, the Astronomer Royal gave an oral explanation of its general subject in the following manner :—

The disturbing effect of Venus upon the moon is not the whole attraction of Venus upon the moon, but the difference of the two attractions, of Venus upon the moon and of Venus upon the earth. Thus, when the moon is between the earth and Venus, the attraction of Venus upon the moon is stronger than that of Venus upon the earth, and therefore it tends to pull Venus away from the earth. When the moon is more distant from Venus than the earth is, the attraction of Venus on the earth is the stronger, and tends to pull it away from the moon, which, in regard to the disturbance of the relative places of the earth and moon, is the same thing as pulling the moon away from the earth. In both these positions, therefore, the disturbing force of Venus tends to pull the moon away from the earth. When the earth and the moon are equally distant from Venus, the attractions of Venus upon the two are equal, but not in parallel lines ; the attractions tend to draw them along the sides of a wedge whose point is at Venus, and, therefore, to diminish the distance between them, or to push the moon *towards* the earth.

Inasmuch as, in one pair of positions of the earth and moon, the disturbing force of Venus tends to increase the distance between them, and in another pair of positions it tends to diminish that distance, it is important to ascertain which of these disturbances is the greater. Suppose the distance of the moon from the earth to be  $\frac{1}{100}$  part of the distance of the earth from Venus. Then, when the moon is between the earth and Venus, its distance from Venus is  $\frac{99}{100}$  of the whole ; the force upon it is  $\frac{10000}{9801}$  of that upon the earth ; the excess of this (or the disturbing force tending to pull the moon away from the earth) is  $\frac{199}{9801}$ , or nearly  $\frac{1}{50}$  of that on the earth. In like manner, when the moon is further from Venus than the earth is, its distance from Venus is  $\frac{101}{100}$  of the earth's distance ; the force upon it is  $\frac{10000}{10201}$  of that upon the earth ; the defect of this (or the disturbing force tending to pull the earth away from the moon) is  $\frac{201}{10201}$ , or nearly  $\frac{1}{51}$  of that on the earth. But when the earth and the moon are at equal distances from Venus, the proportion of their relative approach (as produced by the action of Venus) to the whole effect of Venus upon them, is evidently represented by the inclination of the two lines drawn from them to Venus, or is the same as the proportion of the distance of the moon from the earth, to the distance of the earth from Venus, and is therefore  $\frac{1}{100}$  of the whole. Thus the force tending to pull the moon from the earth at one time is about double the force tending to push the moon towards the earth at another time ; and therefore, upon the whole, the tendency of the

disturbing force of Venus is to pull the moon from the earth. To arrive at this conclusion, we have considered only four points of the moon's orbit: in other points the effects of the perturbation are more complicated; but they do not alter this general conclusion.

The same remark applies to the disturbing effect of Venus upon the moon when at a given point of its orbit, provided the nature of that point be such that at different times it is in all possible positions relative to Venus. For instance, the moon's apogee is (in consequence of the motion of the line of apses, and of the relative motions of the earth and Venus) sometimes between the earth and Venus, sometimes more distant from Venus than the earth is, sometimes  $90^\circ$  to the right, sometimes  $90^\circ$  to the left. We may assert therefore that, upon the whole, the disturbing force of Venus upon the moon, when she is in apogee, tends to draw her away from the earth. The same may be predicated when the moon is in perigee.

Next, it is important to ascertain how the disturbing force depends upon the moon's distance from the earth. For this purpose, instead of supposing, as before, that the moon's distance is  $\frac{1}{100}$  part of the distance of the earth from Venus, let us suppose it  $\frac{2}{100}$  part of that distance. Then when the moon is between the earth and Venus, the force upon the moon is  $\frac{10000}{9604}$  of that upon the earth, and therefore the excess, or the disturbing force, is  $\frac{396}{9604}$ , or nearly  $\frac{1}{25}$  of the whole force upon the earth. In the former assumed instance it was  $\frac{1}{50}$ . Thus, upon doubling the moon's distance from the earth, the disturbing force is doubled. And similarly for other distances of the moon from the earth, the disturbing force (in similar positions with regard to Venus) is proportional to the moon's distance. Thus, when the moon is at apogee, in a given position with regard to Venus, the disturbing force is greater than when the moon is in perigee in the same position. And, upon the whole, in all possible relative positions of the moon and Venus, the action of Venus pulls away the moon from the earth, more when she is in apogee than when she is in perigee.

Now we may consider the general effect of these forces upon the dimensions of the moon's orbit. So long as the force which draws the moon towards the earth is always the same at the same distance, the moon will continue to describe an orbit of the same dimensions over and over again. But if at any time the force directed towards the earth *suddenly* grows smaller, the moon will *immediately* rush off in an orbit which, on the opposite side, is larger. If the force towards the earth *gradually* grows smaller, the dimensions of the orbit will *gradually* increase. And the periodic time in the orbit described at every successive revolution will undergo the change corresponding to the change of dimensions (that is, to the change of major axis) of the orbit, and will therefore become continually greater and greater.

These are the changes which produce the most serious disturbance in the apparent place of the moon. If a force, after acting for a long time, produce a small change in the eccentricity of the moon's orbit, the effect on the moon's place is simply the amount of the corre-

sponding change in the equation of the centre, and cannot possibly exceed that amount. But if the force have been for a long time gradually altering the major axis, and consequently the periodic time in the moon's orbit, then during the whole of that time the moon has been performing her revolutions quicker or slower than we expected, and therefore at the end of that time she is in advance or in retard of her expected place by an amount equal to the accumulation of all the advances or retards in all the revolutions through which the change has been going on. The planetary inequalities of long period are all of this kind. The major axis here plays the same part as the pendulum of a clock. If a small force acting for a year pushed the seconds-hand forwards by an inch, the clock would be merely a few seconds wrong ; but if in the same time it shortened the pendulum by an inch, the clock would have gained fifty hours ; and if the time occupied by the change had been greater, the disturbance in the clock indication would have been proportionably greater.

In order then to find inequalities of long period in the motion of the moon produced by Venus, we must seek for some alternate increase and decrease, occupying a very long period, in the force by which Venus draws the moon from the earth.

No such slow increase and decrease have been found in the general force by which Venus disturbs the moon.

The next point of inquiry is, whether a combination of the changes in the force of Venus with the changes in the position of the moon in its orbit can produce a force, which, for a very long time together, gradually increases the force drawing the moon from the earth, and then for an equal time gradually diminishes that force.

A force which acts in opposite ways, nearly on opposite sides of the moon's orbit (pulling the moon from the earth on one side and pushing it towards the earth on the other side), may produce this effect, provided the period of the change in the nature of the force (from pulling to pushing) correspond *nearly*, but *not exactly*, with the time in which the moon moves from apogee to perigee. For (as we have seen) the effect of a certain force of Venus is to produce a greater disturbing force on the moon at apogee than at perigee ; and this force, or a change in this force, will, at apogee, produce a greater effect on the dimensions of the moon's orbit than at perigee, both because the disturbing force is actually greater, and because it acts on the moon when the moon's velocity is smaller. Therefore, if a pulling force, gradually increasing in magnitude, act on the moon at apogee, it will gradually increase the dimensions of the moon's orbit : if a corresponding pushing force act at perigee, it will gradually diminish the dimensions of the moon's orbit ; but the former prevails, and the orbit will gradually increase in size. If after a time the pulling force at apogee gradually diminish, and at length become a pushing force, while the pushing force at perigee gradually diminishes, and at length becomes a pulling force, then the orbit will gradually diminish in size. And this change of forces would be produced by such a modification in Venus's force, as that

of which we have spoken, namely, a force which acts in opposite ways on opposite sides of the moon's orbit, and in which the period in the change of the nature of the force coincides *nearly*, but *not exactly*, with the time in which the moon moves from apogee to perigee; for then the pulling force at apogee will after a long time be changed to a pushing force, and the pushing force at perigee will in the same time be changed to a pulling force. If, for instance, the change in the disturbing forces of Venus (from pushing to pulling) occupied fourteen days exactly, and if the moon's motion from apogee to perigee occupied fourteen days and five minutes, then in 4032 anomalistic semi-revolutions of the moon (which would bring her from apogee to apogee), there would have been 4033 changes of the force (which would change it from pulling to pushing), and therefore in this time, and no sooner, a complete pulling force at apogee would be changed to a complete pushing force at apogee.

It is necessary now to point out how such a modification of the force of Venus can be found.

The only disturbing forces which are yet completely brought under the management of mathematicians are of two kinds; a constant force (always pushing or always pulling with the same amount of force), and a force alternately pushing and pulling, having equal periods and equal maximum magnitudes in each state. The latter of these, if projected graphically, with the time for abscissa, is represented by the ordinates of a *line of sines*: algebraically, it is expressed by  $a \cos(bt+c)$ .

Now, while the relative positions of the earth and Venus change, the disturbing force on the moon (estimated by the force which, on the whole, it exerts to pull the moon from the earth) undergoes very great changes. When Venus is nearest to the earth, this force is about 250 times as great as when Venus is furthest from the earth. It declines very rapidly from its greatest magnitude. If therefore we represent the disturbing force from one conjunction to the next by a curve, this curve will be very high at the beginning and end, and very near the line of abscissa at the middle, and through the greater part of its extent.

The separation of this force into a number of different forces, following the two laws mentioned above, is effected by a process suggested and facilitated by algebra, but in which, nevertheless, every step has its physical meaning. It may be stated at once, that this remark applies universally to the algebraical operations of physical mathematics. As a simple instance, we may refer to the equation  $(a+b)^3 = a^3 + 3a^2b + 3ab^2 + b^3$ , which probably was suggested by algebra; but which may be illustrated by taking a cube, whose side is  $a+b$ , and (by three saw-cuts) cutting it into eight pieces, when the single piece representing  $a^3$ , the three pieces each representing  $a^2b$ , the three pieces each representing  $ab^2$ , and the single piece representing  $b^3$ , will be found. And there is perhaps no better discipline for the mind than thus tracing the evidence of the truth of algebra, especially in its more profound processes.

The separation, then, of the force of Venus goes on by the following steps:—

1st. A constant pulling force, equal to the mean value of the force.

2nd. A force pulling when Venus is in conjunction, pushing at the time intermediate to the conjunctions, and pulling when Venus is in conjunction again; thus going completely through its changes *once* between conjunction and conjunction.

3rd. A force pulling when Venus is in conjunction, then pushing, &c., going through its changes *twice*.

4th. A force pulling when Venus is in conjunction, then pushing, &c., going through its changes *thrice*.

In this manner the forces go on, continually diminishing in magnitude. When we arrive at the 18th, the force is extremely small.

The algebraical expression for the collection of these terms, putting  $\theta$  for the difference of mean longitude of the earth and Venus, is

$$A + B \cdot \cos \theta + C \cdot \cos 2\theta + D \cdot \cos 3\theta + \text{&c.}$$

This is on the supposition that the orbits of the two planets are circular and in the same plane. But, in consequence of their eccentricities and inclinations, the forces of any one system alternately pushing and pulling (Nos. 2, or 3, or 4, &c.) will not have the same *maximum* magnitude throughout. But each can, in all cases, be expressed by the combination of three such forces, in each of which the maximum forces are equal throughout. Thus, if we combine a large force, going through its changes twenty times in a certain period, with a small force going through its changes nineteen times in the same period, and another small force going through its changes twenty-one times in the same period, then it will be found that both the small forces increase the large force (whether in its pulling or in its pushing state) near the beginning and the end of the time; that both diminish the large force near the middle of the time; and that the two small ones destroy each other at a quarter and three-quarters of the time. The effect of this combination is therefore precisely such as is spoken of above.

Thus, then, for the complete expression of the force, we are driven to an infinite number of forces following the law of alternately pulling and pushing, but with very great variety of magnitudes of force and of periodic time. The greatest portion of these produce no sensible effect; some because (though their magnitudes are large) they act for so short time in one way, or their periods are so little related to the periods of any movement of the moon, that their effects never accumulate; others because their magnitudes are small, and there is no unusual circumstance favourable to their increase.

But there is one of these forces which, in the algebraical expression, depends on  $18 \times$  mean longitude of Venus —  $16 \times$  mean longitude of the earth, whose coefficient is exceedingly small, but which goes through all its changes, from pulling to pulling again, in the time,

$$27^d 13^h 7^m 35^{s.6};$$

or from pulling to pushing, in the time

$$13^d 18^h 33^m 47^{s.8}.$$

Now, the anomalistic revolution of the moon, from apogee to apogee again, is performed in the time

27<sup>d</sup> 13<sup>h</sup> 18<sup>m</sup> 32<sup>s</sup>.3;

or from apogee to perigee, in the time

13<sup>d</sup> 18<sup>h</sup> 39<sup>m</sup> 16<sup>s</sup>.1.

Here we have a real instance, exactly corresponding to the case which, for the sake of explanation, we assumed a short time back, and the results are truly such as were there described. During about 4000 half-revolutions of the moon, or 2000 revolutions, the pulling force at apogee is gradually diminishing till it becomes a pushing force, and during about 2000 more revolutions, the pushing force at apogee is gradually diminishing till it becomes again a pulling force; the opposite changes going on in the force at perigee: and thus, for reasons fully explained before, the moon's orbit is gradually contracting during 2000 revolutions, and gradually expanding during 2000 revolutions more. And although the change in the size of the orbit is totally insensible in observation (for, according to a rough calculation, the utmost accumulation of change in the major axis of the moon's orbit is only ten *feet*, sometimes in increase and sometimes in decrease), yet the consequent alteration in its periodic time, continued through so many revolutions, is sufficient to cause the irregularity in question. The inequality in longitude, as measured on the moon's orbit, exceeds thirty *miles*, sometimes in advance, and sometimes in retard.

For a complete understanding of this matter, it must carefully be borne in mind that the force at the apogee, which has been described as a pushing force through 136 years, is not absolutely a pushing force through every month of that time, but that (in consequence of the motion of the moon's line of apses) if we take any period of nine or ten years, the moon's apogee will in that time have passed through every position with regard to Venus, and therefore, *upon the whole*, during that period of nine or ten years, the force at apogee will have been a pushing force. In like manner, in another period of 136 years, if we take any period of nine or ten years, *upon the whole*, during that period of nine or ten years, the force at apogee will have been a pulling force.

The general cause of the inequality depending on the argument  $8g'' - 13g'$ , has been sufficiently stated in one of the last paragraphs of the abstract of M. Hansen's paper.

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### LXIII. *Intelligence and Miscellaneous Articles.*

#### ON THE GELATINOUS SUBSTANCES OF VEGETABLES.

**M.** FREMY, in a memoir read before the Academy of Sciences, has arrived at the following conclusions:—

1st. There exists in vegetables, along with cellulose, a substance which is insoluble in water, alcohol and æther, which the author

names *pectose*, and which, by the action of the weakest acids, is converted into pectin. Diluted acids produce this effect only at the temperature of ebullition; and acetic acid, which, as is well known, does not act upon starch, is also without action on pectose. Pectose cannot be confounded with cellulose, for the latter, as was ascertained by M. Payen, gives no traces of pectin when treated with acids. M. Fremy's experiments confirm those of M. Payen.

2nd. The author has found in the greater number of fruits and roots, an amorphous substance, comparable to ferments, and especially to diastase: the gelatinous substances contained in vegetables experience by its action a series of isomeric transformations. This substance M. Fremy calls *pectase*; in acting upon the gelatinous substances it gives rise to the different phenomena which constitute pectic fermentation.

3rd. The acids which are employed to convert pectose into pectin, may, according to their nature and proportion, form different substances, each of which possesses well-defined distinctive properties. Thus, when the acid is very weak, pectin, properly so called, is obtained, which does not render acetate of lead turbid. If the acid be more concentrated, or if the ebullition has been longer continued, the substance formed precipitates the neutral acetate of lead; this substance the author calls *parapectin*; and lastly, by employing a powerful acid, a third substance may be formed, which is distinguished by the name of *metapectin*; this is feebly acid to coloured test-papers, and precipitates chloride of barium; the other compounds are neutral.

4th. If a small quantity of pectase be added to a solution of pectin, and the temperature be kept at about 86° F., the pectin is soon observed to change into a gelatinous, consistent substance. This curious transformation, which explains the production of vegetable jellies, may be effected without the contact of the air; there are formed in this case two acids; one is new, and termed *pectosic acid*, and the other is pectic acid. Pectosic acid, which might be confounded with pectic acid, is immediately distinguishable from it by its perfect solubility in boiling water. In the reaction of pectase on pectin, pectosic acid is first produced, and is afterwards changed into pectic acid by the prolonged action of the pectase. The free alkalies or their carbonates are capable of converting in the cold, pectin at first into pectosates and afterwards into pectates.

The phenomena now described are so easy of observation, according to M. Fremy, and characterize pectin so distinctly, that he finds it difficult to imagine how in later times pectin has been confounded with gums, mucilages, and especially with pectic acid, which is insoluble in water.

The author has particularly examined pectic acid, and is of opinion that he has overcome the difficulties attendant upon its analysis, and especially the determination of its equivalent. He has also found that pectic acid, heated to 392° F., loses water and carbonic acid, and a new pyrogenous acid, which he calls *pyropectic acid*, is produced.

Pectic acid possesses the singular property of dissolving in considerable quantity in neutral or acid salts; it then forms compounds precipitable as jellies by alcohol; these precipitates are often mixed with pectin, render it gelatinous, and prevent by their presence the recognition, by means of elementary analysis, of the simple relations which connect pectin with the other gelatinous bodies.

5th. The gelatinous bodies may undergo a last period of transformation, and be changed into two very soluble and energetic acids. It is sufficient to boil pectic acid in water for a certain time to convert it into an acid, called by the author *parapectic acid*, and into another acid termed *metapectic acid*. The parapectic and metapectic acids are also formed during the action of acids or alkalies on pectin or pectic acid: the pectates may by long boiling be converted into metapectates. These two acids are readily distinguished from each other; for the first precipitates barytes water, and the second does not; they decompose the double tartrate of copper and potash, as glucose does. To be certain that this property was not derived from the presence of sugar, the author had recourse to a polarizing apparatus and the action of yeast. Guided by the advice of M. Biot, M. Fremy found that the parapectic and metapectic acids effected no rotary action on polarized light, and that the presence of yeast produced no traces of fermentation.

6th. After having examined all the properties of the gelatinous bodies, and found that by employing very weak agents, comparable to those which exist in vegetables, their acidity might be successively developed, and from neutral bodies, which they originally were, they might be transformed into energetic acids, the author examined whether, during the act of vegetation, gelatinous substances did not undergo changes comparable to those which he had produced artificially. On following for two years, with this intention, the modifications which are effected in fruits during their maturation, M. Fremy found that the gelatinous bodies which occur in them could pass through the different intermediate states which he has described; thus green fruits contain abundance of pectose. As maturation advances the pectose is changed into pectin; and when the fruits are perfectly ripe, the pectin is frequently completely converted into metapectic acid. The modifications examined in this memoir are then precisely those which occur during the maturation of fruits.

The author found in the numerous analyses which he performed that the composition of the gelatinous bodies could not be represented by carbon and water, and consequently that they were far removed from neutral bodies, properly so called. As experiment always indicates a larger quantity of hydrogen than really exists in organic bodies, the author states that he cannot attribute the difference which he has obtained to an error of analysis.

The table presented to the Academy shows that all gelatinous substances, similar to those which are derived from starch, are isomeric, or at least they differ only by the elements of water. This

result might be foreseen ; for when a mixture of pectase and pectin is put into a bottle, and it is hermetically sealed, the pectin is successively converted into pectosic, pectic, parapectic, and metaplectic acids, without forming any secondary product.

The capacities of saturation given in the following table prove that the acidity of the gelatinous bodies increases in proportion as their equivalent diminishes. Thus parapectin, the equivalent of which is very heavy, forms a neutral salt with lead which contains 10 per cent. of oxide, and does not redden tincture of litmus ; and metaplectic acid, the equivalent of which is very light, produces a salt of lead which contains 67 of oxide, and its acidity resembles that of malic or citric acid.

Names of the gelatinous substances.	Composition of the gelatinous substances.	Composition of the salts of lead.
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Pectose

Pectin.....	$C^{64} H^{40} O^{56}, 8HO$	$C^{64} H^{40} O^{56}, 7HO, PbO$
Parapectin .....	$C^{64} H^{40} O^{56}, 8HO$	$C^{64} H^{40} O^{56}, 6HO, 2PbO$
Metapectin.....	$C^{64} H^{40} O^{56}, 8HO$	$C^{64} H^{40} O^{56}, HO, 2PbO$
Pectosic acid ....	$C^{32} H^{20} O^{28}, 3HO$	$C^{32} H^{20} O^{28}, HO, 2PbO$
Pectic acid .....	$C^{32} H^{20} O^{28}, 2HO$	$C^{32} H^{20} O^{28}, 2PbO$
Parapectic acid ..	$C^{24} H^{15} O^{21}, 2HO$	$C^{24} H^{15} O^{21}, 2PbO$
Metaplectic acid ..	$C^8 H^5 O^7, 2HO$	$C^8 H^5 O^7, 2PbO$

M. Fremy states that the formula of pectic acid, which he has here adopted, gives in 100 parts exactly the same quantities as determined by M. Regnault, and as published by himself in his first memoir on gelatinous bodies.

The author concludes that he has succeeded in proving that vegetables contain a neutral insoluble substance, which is convertible during vegetation into an energetic acid.—*Comptes Rendus*, Juin 14, 1847.

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#### PREPARATION OF PROTOXIDE OF TIN.

M. Roth gives the following process for preparing the red protoxide of tin :—The white hydrate is to be prepared, and after being well-washed it is to be digested at  $133^{\circ}$  F. in a solution of protacetate of tin, with a slight excess of acid, and of specific gravity about 1·06. The protoxide is then converted into hard heavy grains, which yield a greenish-brown powder ; these grains inflame when heated, and readily blacken in the sunshine. They behave with reagents like common protoxide.—*Journ. de Ph. et de Ch.*, Août 1847.

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#### [ON THE PRESENCE OF ARSENIC, COPPER AND TIN, IN THE MINERAL WATERS OF BAVARIA.]

According to the experiments of M. Buchner, Jun., the brownish-yellow ochrey deposit of the springs of Ragoczy and of Pandour, at Kissingen, contain only doubtful traces of copper ; but they con-

tain sufficient quantities of arsenic to admit of the extraction of the metal.

The reddish-brown ochre of the ferruginous spring of Brücknau contains mere traces of arsenic, but there is much copper. Tin has been discovered in the ochres of Kissingen and of Brücknau. Experiments performed to ascertain the presence of arsenic and copper in the brownish-yellow ochre of the ferruginous waters of Kellberg were not followed by any positive results.—*Journ. de Ph. et de Ch.*, Août 1847.

#### SOLUBILITY OF COMMON SALT IN ALCOHOL.

M. Wagner has determined the degree of solubility of chloride of sodium in alcohol of different densities and at various temperatures. The results are that—

Alcohol of 75 per cent.	dissolves at 57°20 F.	0·661 part of salt.
.... 75	.... 59·45	0·700 ....
.... 75	.... 100·40	0·736 ....
.... 75	.... 160·70	1·033 ....
.... 95·5	.... 59·0	0·174 ....
.... 95·5	.... 171·05	0·171 ....

*Ibid.*

#### ON SOME IMPROVED FORMS OF CHEMICAL APPARATUS.

BY THOMAS TAYLOR, ESQ.

Among the many advantages possessed by the Chemical Society, it appears to me not the least, that it affords to its members a ready mode of communicating to one another many of those little practical facts and modes of operating, which, although perhaps not of sufficient importance to merit distinct notice in the scientific journals, are nevertheless of considerable value to those engaged in the prosecution of the science. In furtherance of this view I will therefore describe some new forms of apparatus which I have myself been in the habit of using for some time past.

The first of these is a mode of closing the mouths of gas-bottles, or indeed of any wide-mouthed vessel into which tubes are to pass, as in Woolf's apparatus, gas generators, &c. To effect this the top of the bottle is first to be slightly ground, so as to procure a level surface, a piece of sheet caoutchouc is then laid upon it, and this is covered by a disc of wood of the same size as the top of the bottle, and from a quarter to half an inch in thickness. The wooden cover is held in its place by means of a small double clamp of brass or of varnished sheet iron, which passes across the cover, and the ends of which are bent under the rim of the bottle, against which they are pressed by a screw fixed in the centre of the clamp. By turning the screw the caoutchouc is sufficiently compressed to render the joint perfectly air-tight. The tubes intended to pass into and out

of the bottle are cemented into the wooden cover, usually on one side of the clamp; and they pass of course through corresponding holes in the caoutchouc. By making these holes somewhat smaller than the diameter of the tubes, the caoutchouc contracts so closely around them, that not only is any liquid which might be accidentally thrown up effectually prevented from getting between the caoutchouc and the wooden cover, but the necessity of cementing the tube into the cover may be even dispensed with. This method is so effectual and easily arranged, that I am quite convinced it will supersede the use of corks in the preparation of all gases which only require the application of a moderate heat and do not act upon caoutchouc. Ground glass plates might of course be substituted where caoutchouc is inapplicable, or a sheet of ground glass might be cemented upon the lower part of the wooden cover; but these modes would be rather expensive, and the cases in which they would be required are not very numerous. In small bottles the use of a clamp is not essential, as sufficient pressure may be obtained by inserting two wedges of wood beneath a string tied around the neck, and over the top of the bottle.

Fig. 1.

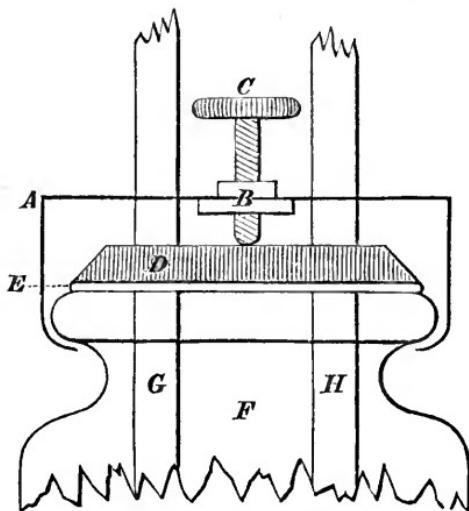


FIG. 1. A clamp of sheet iron having a small centre of brass B, in which the screw C works. D disc of wood. E sheet of caoutchouc. F glass bottle. G H glass tubes.

I will next direct the attention of the Members to a new mode of cupelling, or rather to a new form of muffle. Cupellation is an operation not often performed by amateurs, chiefly I believe on account of the difficulty in doing it unless provided with furnaces built expressly for the purpose. The following plan I have found to afford most accurate results, while it may be performed in almost any furnace:—The mouths of two black lead crucibles of the same size are to be ground flat, so that when applied one to the other they may stand quite steady. An oblong or semicircular notch is to be cut out of the mouth of one of the crucibles, and a hole is also to be

drilled through its bottom. This crucible when placed upon the top of the other constitutes the muffle, and of course resembles in shape a skittle. To cupel with this apparatus, the lower crucible is nearly filled with clean sand, set upon the bars of the grate in the centre of the furnace, and brought to a low red heat. The cupel containing the lead and the alloy is then placed upon the sand and immediately covered by the other crucible, taking care that the notch in its side shall be opposite to, and correspond with the furnace-door; more fuel is added, during which it is well to cover the hole in the top of the muffle with a crucible lid, in order to prevent the admission of dirt. When the muffle has become throughout of a bright red heat, the furnace-door is thrown open, and the ignited fuel gently moved aside, so as to permit a view of the side opening in the muffle. The current of air which is thus established through the muffle instantly causes rapid oxidation of the lead, and this may be regulated at pleasure by closing the door more or less. If from the fuel falling down any difficulty should be experienced in maintaining a free passage for the air, a portion of a porcelain tube or a gun-barrel may be passed through the furnace-door to within an inch of the muffle; but this proceeding is generally rendered quite unnecessary by taking care to place some large pieces of coke immediately around the door of the furnace.

In many cases it will be found advantageous to convert the lower crucible itself into the cupel by first half-filling it with sand and then ramming in pounded bone-earth. I have found the above method to possess the following advantages:—In the first place, the crucibles may be maintained at a much higher temperature than can be readily obtained when the ordinary muffle is used, while the degree of heat and the quantity of air admitted may be regulated with the greatest nicety. Secondly, owing to the greater draught of air, the oxidation of the lead is more quickly effected; and lastly, by looking through an opening in the furnace cover, the operation may be watched from first to last.

Fig. 2.

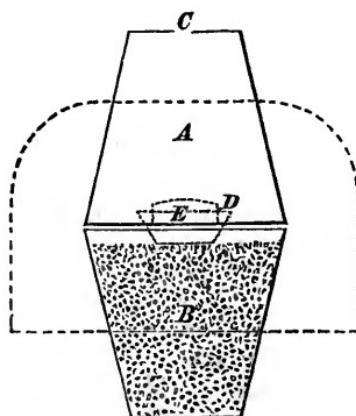
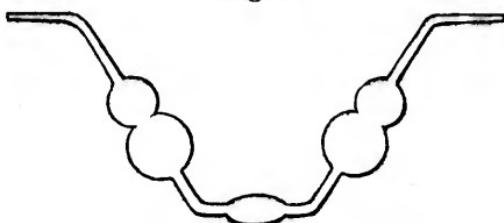


FIG. 2. A B black lead crucibles. C the upper opening. D the lower opening. E the cupel. The dotted semicircle represents the position of the furnace-door.

*Improved Form of Messrs. Will's and Varrentrapp's Apparatus.*

The only inconvenience I have found in the process proposed by Drs. Will and Varrentrapp for the estimation of nitrogen in organic bodies, is the liability of the liquid in the condenser being thrown back into the combustion-tube by sudden absorption taking place, or from too violent an evolution of the gases, part of it being ejected from the other extremity of the condenser. So well-aware were its authors of this inconvenience, that they recommend in the analyses of substances rich in nitrogen the introduction of sugar, or some other body abounding in carbon, into the combustion-tube. I have found that the necessity of this addition, which is of course open to many objections, may be entirely avoided by using a condenser nearly three times as large as that generally employed, and by surmounting each of the bulbs with another bulb of about half its capacity. The opening between the bulbs should be very wide, they being run into one another in the same manner as in the lower bulbs of Liebig's potash apparatus. With a condenser of this description, the large bulbs being  $1\frac{1}{4}$  inch in diameter and about 4 inches apart, I have never experienced the least accident, nor am I compelled to pay that constant attention to the progress of the combustion which Drs. Will's and Varrentrapp's condenser usually requires.

Fig. 3.



Mr. Taylor also exhibited a small instrument for holding Daguerréotype plates during the process of washing off. It consisted of two pieces of brass or plaited wire fitted into a wooden handle. One of the wires is bent into the form of an acute triangle, its base being slightly turned up, so as to form a ledge for the silver plate to rest upon. The other wire is placed between the sides of the triangle curved, so as to form a spring, which rests upon the top of the plate, and keeps it in its place. By inserting the fore-finger in the loop of the spring, the plate may be shaken violently without becoming dislodged.

Fig. 4.



*From the Proceedings of the Chemical Society.*

## PREPARATION AND COMPOSITION OF LIGNIN.

MM. Poumarède and Figuer state as a test of the purity of lignin, that when immersed in concentrated sulphuric acid it is not rendered black. In order to procure it in this state, a piece of wood is to be transversely rasped, and the raspings are to be immersed in soap ley for twenty-four hours; the mixture is then to be diluted with once or twice its weight of water and poured off; the insoluble residue is to be largely washed with water, treated with a slight excess of dilute hydrochloric acid, and again washed with water. After this the ligneous fibre is to be treated with great excess of a solution of common salt; the digestion is to be continued with occasional stirring for two or three days, a fresh portion of the solution being once used; this being poured off, the fibrous matter is to be treated with a weak alkaline solution till it comes away colourless; it is to be again washed, and the remaining alkali is to be saturated by slight excess of hydrochloric acid, and after again washing with distilled water till litmus is not reddened, the product, placed on a sieve, is to be dried either in the sun or a stove.

The lignin thus obtained, after being washed with alcohol and æther, is not coloured by concentrated sulphuric acid, and is to be considered as absolutely pure. It is white and silky, and possesses the organic structure of the wood from which it has been obtained; and the authors consider themselves authorized to conclude that in analysing this substance, they operate on the vegetable skeleton such as it exists in plants.

The authors find that the results of their analyses differ but very little from those obtained by M. Payen; they nevertheless deem it necessary to state them as satisfactorily proving the agreement which exists between the various kinds of lignin of very different origin.

Lignin of the poplar, dried at 288° F.; mean of three experiments:—

Carbon .....	43·88
Hydrogen .....	6·23
Oxygen .....	49·89
<hr/>	
	100·00

Lignin of the beech, dried at 288° F.:—

Carbon .....	43·85
Hydrogen .....	6·22
Oxygen .....	49·93
<hr/>	
	100·00

Blotting-paper treated with acids, alkalies, water, and alcohol, dried at 288° F.:—

	I.	II.
Carbon .....	43·87	43·84
Hydrogen.....	6·12	6·22
Oxygen .....	50·01	49·94
	<hr/>	<hr/>
	100·00	100·00

Cotton treated only with boiling water, hydrochloric acid, and dilute solution of potash, cold :—

	I.	II.
Carbon.....	43·46	43·10
Hydrogen....	6·38	6·43
Oxygen .....	50·16	50·45
	<hr/> 100·00	<hr/> 99·98

Flax, treated like cotton :—

	I.	II.
Carbon.....	43·92	43·33
Hydrogen.....	6·01	6·41
Oxygen .....	50·07	50·26
	<hr/> 100·00	<hr/> 100·00

*Papyrin.*—In employing sulphuric acid to determine the purity of lignin, the authors have discovered a new substance which constitutes a very curious modification of ligneous tissues. It results from the first action of sulphuric acid on lignin, and is the product which arises before its conversion into dextrin.

Let blotting-paper be immersed for not more than half a minute in concentrated sulphuric acid, and then be immediately washed with a large quantity of water to prevent the action of the acid; and if it be then immersed for a few moments into water containing a few drops of ammonia, a substance is obtained which possesses all the physical characters of an animal membrane. When moistened with water, it has the soft and greasy feel of animal membrane softened in water; when dried it has the appearance and the toughness of parchment, and when glazed it has considerable transparency.

This substance, which the authors call *papyrin*, is identical in composition with lignin. It was found to yield—

	I.	II.	III.
Carbon .....	43·30	43·89	44·44
Hydrogen....	6·28	6·27	6·23
Oxygen ....	50·42	49·84	49·33
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

*Journ. de Ph. et de Ch.*, Août 1847.

#### SOLUBILITY OF CHLORIDE OF SILVER IN HYDROCHLORIC ACID.

M. Pierre states that concentrated hydrochloric acid is capable of dissolving  $\frac{1}{200}$ dth of its weight of chloride of silver; when it has been diluted with twice its weight of water, it is capable of retaining more than  $\frac{1}{600}$ dth of its weight.

M. Gerhardt observes that this fact is important, and says he had previously stated it; and it appears to him to be the cause of the difference of the numbers obtained by MM. Berzelius and Marignac as to the theoretical number expressing the atomic weight of chlorine according to Dr. Prout's law of multiples.—*Ibid.* Sept. 1847.

*Daubeny on Active and Extinct Volcanos.*

Professor Daubeny of Oxford has in the press, and nearly ready for publication, a new and much-enlarged edition of his Description of Active and Extinct Volcanos.

The present Edition will be found to contain nearly twice the amount of matter included in the preceding one, embracing not only such new facts and observations with respect to volcanos as have been brought to light since its first appearance in 1826, but likewise the allied phenomena of Earthquakes and Thermal Springs, as well as a fuller discussion of the theories connected with those subjects.

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## METEOROLOGICAL OBSERVATIONS FOR SEPT. 1847.

*Chiswick*.—September 1. Clear : cloudy : clear. 2. Cloudy : boisterous. 3. Cold rain : overcast. 4. Fine. 5. Clear : shower : clear. 6. Very fine. 7. Clear and cold : cloudy : rain at night. 8. Rain. 9. Very fine. 10. Overcast : very fine. 11, 12. Very fine. 13. Densely overcast : rain. 14. Very fine : slight shower : clear and cold at night. 15. Fine : boisterous, with rain at night. 16. Boisterous. 17. Rain. 18. Cloudy, with very clear intervals. 19. Cloudy : heavy rain at night. 20. Fine : slight showers. 21. Rain. 22. Cloudy : fine. 23. Cloudy and mild. 24. Foggy : very fine. 25, 26. Fine. 27. Frosty : clear : very fine : clear and frosty at night. 28. Slight fog : overcast. 29. Slight fog : very fine. 30. Dry haze : overcast.

Mean temperature of the month .....	59° 40
Mean temperature of Sept. 1846 .....	60° 79
Mean temperature of Sept. for the last twenty years .....	52° 77
Average amount of rain in Sept. .....	2·73 inches.

*Boston*.—Sept. 1. Fine. 2. Windy. 3. Cloudy : rain p.m. 4. Fine. 5. Fine : rain p.m. 6, 7. Fine. 8. Cloudy. 9—11. Fine. 12. Windy. 13. Rain : rain a.m. and p.m. 14. Fine. 15. Fine : rain p.m. 16. Fine : stormy from 10 a.m. 17. Cloudy. 18—20. Fine. 21. Fine : rain p.m. 22. Cloudy : rain a.m. 23. Cloudy. 24—28. Fine. 29. Cloudy. 30. Fine.

*Sandwick Manse, Orkney*.—Sept. 1, 2. Showers. 3. Bright : showers : sleet. 4—6. Showers. 7, 8. Cloudy : showers. 9. Drizzle : showers. 10. Cloudy. 11. Cloudy : rain. 12. Showers. 13. Cloudy : clear. 14. Cloudy. 15, 16. Bright : rain. 17. Cloudy : showers. 18. Showers. 19. Clear : showers : sleet. 20. Showers : rain : cloudy. 21. Bright : fine. 22. Damp : rain. 23. Showers. 24. Showers : cloudy. 25. Rain : clear. 26. Bright : clear. 27, 28. Clear. 29. Clear : aurora. 30. Clear.

*Applegarth Manse, Dumfries-shire*.—Sept. 1. Sharp showers and high wind. 2. Clear and fine harvest day. 3. Rain. 4. Fine clear sharp weather. 5. Fine harvest day. 6. Clear and bracing. 7. Rain, though not heavy. 8. Fair, but cloudy. 9. Close rain. 10. Fine : some drops p.m. 11. Fair a.m. : rain p.m. 12. Fair, but threatening. 13. Fine. 14. Bracing day : flying showers. 15. Fine a.m. : heavy rain p.m. 16. Rain and high wind. 17. Few drops of rain. 18. Fair, but dull. 19. Frequent showers. 20. A few drops. 21. Rain p.m. 22, 23. Showery. 24. Fair and fine. 25. Slight drizzle. 26. Very fine day. 27. Very fine day : frost a.m. 28, 29. Very fine days : no frost. 30. Fair, but cold.

Mean temperature of the month .....	50° 9
Mean temperature of Sept. 1846 .....	59° 6
Mean temperature of Sept. for 25 years .....	55° 2
Mean rain in Sept. for 20 years .....	3·13 inches.

*Meteorological Observations made by Mr. Thompson at the Garden of the Horticultural Society at Chiswick, near London; by Mr. Yeall, at Boston; by the Rev. W. Dunbar, at Applegarth Manse, DUMFRIES-SHIRE; and by the Rev. C. Clouston, at Sandwick Manse, ORKNEY.*

THE  
LONDON, EDINBURGH AND DUBLIN  
**PHILOSOPHICAL MAGAZINE**  
AND  
**JOURNAL OF SCIENCE.**

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[THIRD SERIES.]

*DECEMBER 1847.*

LXIV. *On the Diamagnetic conditions of Flame and Gases.*  
By MICHAEL FARADAY, F.R.S., *Foreign Associate of the  
Academy of Sciences, &c.*

*To Richard Taylor, Esq.*

Royal Institution,  
Nov. 8, 1847.

MY DEAR SIR,  
I LATELY received a paper from Professor Zantedeschi, published by him, and containing an account of the discovery, by P. Bancalari, of the magnetism (diamagnetism) of flame, and of the further experiments of Zantedeschi, by which he confirms the result, and shows that flame is repelled from the axial line joining two magnetic poles. I send you the paper that you may, if you estimate its importance as highly as I do, reprint it in the Philosophical Magazine; and I send also with it these further experimental confirmations and extensions of my own. As M. Zantedeschi has published his results, I have felt myself at liberty to work on the subject, which of course interested me very closely. Probably what I may describe will only come in confirmation of that which has been done already in Italy or elsewhere; and if so, I hope to stand excused; for a second witness to an important fact is by no means superfluous, and may in the present case help to induce others to enter actively into the new line of investigation presented by diamagnetic bodies generally.

I soon verified the chief result of the diamagnetic affection of flame, and scarcely know how I could have failed to observe the effect years ago. As I suppose I have obtained much more striking evidence than that referred to in Zantedeschi's paper, I will describe the shape and arrangement of the essential parts of my apparatus. The electro-magnet used was the powerful one described in the Experimental Researches (2247\*). The two terminal pieces of iron forming the virtual magnetic poles were each 1·7 inch square and six inches long;

\* Page 398 of this Journal for May 1846.

but the ends were shaped to a form approaching that of a cone, of which the sides have an angle of about  $100^{\circ}$ , and the axis of which is horizontal and in the upper surface of the pieces of iron. The apex of each end was rounded; nearly a tenth of an inch of the cone being in this way removed. When these terminations are brought near to each other, they give a powerful effect in the magnetic field, and the axial line of magnetic force is of course horizontal, and on a level nearly with the upper surface of the bars. I have found this form exceedingly advantageous in a great variety of experiments.

When the flame of a wax taper was held near the axial line, but on one side or the other, about one-third of the flame rising above the level of the upper surface of the poles, as soon as the magnetic force was on, the flame was affected; and receded from the axial line, moving equatorially, until it took an inclined position, as if a gentle wind was causing its deflection from the upright position; an effect which ceased the instant the magnetism was removed.

The effect was not instantaneous, but rose gradually to a maximum. It ceased very quickly when the magnetism was removed. The progressive increase is due to the gradual production of currents in the air about the magnetic field, which tend to be, and are, formed on the assumption of the magnetic conditions, in the presence of the flame.

When the flame was placed so as to rise truly across the magnetic axis, the effect of the magnetism was to compress the flame between the points of the poles, making it recede in the direction of the axial line from the poles towards the middle transverse plane, and also to shorten the top of the flame. At the same time the top and sides of the compressed part burnt more vividly, because of two streams of air which set in from the poles on each side directly against the flame, and then passed out with it in the equatorial direction. But there was at the same time a repulsion or recession of the parts of the flame from the axial line; for those portions which were below did not ascend so quickly as before, and in ascending they also passed off in an inclined and equatorial direction.

On raising the flame a little more, the effect of the magnetic force was to increase the intensity of the results just described, and the flame actually became of a fish-tail shape, disposed across the magnetic axis.

If the flame was raised until about two-thirds of it were above the level of the axial line, and the poles approached so near to each other (about  $0\cdot3$  of an inch) that they began to cool and compress the part of the flame at the axial line, yet without interfering with its rising freely between them; then,

on rendering the magnet active, the flame became more and more compressed and shortened; and as the effects proceeded to a maximum, the top at last descended, and the flame no more rose between the magnetic poles, but spread out right and left on each side of the axial line, producing a double flame with two long tongues. This flame was very bright along the upper extended forked edge, being there invigorated by a current of air which *descended* from between the poles on to the flame at this part, and in fact drove it away in the equatorial direction.

When the magnet was thrown out of action, the flame resumed its ordinary upright form between the poles, at once; being depressed and redivided again by the renewal of the magnetic action.

When a small flame, only about one-third of an inch high, was placed between the poles, the magnetic force instantly flattened it into an equatorial disc.

If a ball of cotton about the size of a nut be bound up by wire, soaked in aether and inflamed, it will give a flame six or seven inches high. This large flame rises freely and naturally between the poles; but as soon as the magnet is rendered active, it divides and passes off in two flames, the one on one side, and the other on the other side of the axial line.

Such therefore is the general and very striking effect which may be produced on a flame by magnetic action, the important discovery of which we owe to P. Bancalari.

I verified the results obtained by M. Zantedeschi with different flames, and found that those produced by alcohol, aether, coal-gas, hydrogen, sulphur, phosphorus, and camphor were all affected in the same manner, though not apparently with equal strength. The brightest flames appeared to be most affected.

The chief results may be shown in a manner in some respects still more striking and instructive than those obtained with flame, by using a smoking taper. A taper made of wax, coloured green by verdigris, if suffered to burn upright for a minute and then blown out, will usually leave a wick with a spark of fire on the top. The subdued combustion will however still go on, even for an hour or more, sending up a thin dense stream of smoke, which, in a quiet atmosphere, will rise vertically for six or eight inches; and in a moving atmosphere will show every change of its motion, both as to direction and intensity. When the taper is held beneath the poles, so that the stream of smoke passes a little on one side of the axial line, the stream is scarcely affected by the power of the magnet, the taper being three or four inches below the poles; but if the taper be raised, so that the coal is not more than an inch

below the axial line, the stream of smoke is much more affected, being bent outwards; and if it be brought still higher, there is a point at which the smoke leaves the taper-wick even in a horizontal direction, to go equatorially. If the taper be held so that the smoke-stream passes *through* the axial line, and then the distances be varied as before, there is little or no sensible effect when the wick is four inches below: but being raised, as soon as the warm part of the stream is between the poles, it tends to divide; and when the ignited wick is about an inch below the axial line, the smoke rises vertically in one column until about two-thirds of that distance is passed over, and then it divides, going right and left, leaving the space between the poles clear. As the taper is slowly raised, the division of the smoke descends, taking place lower down, until it occurs upon the wick, at the distance of 0·4 or 0·5 of an inch below the axial line. If the taper be raised still more, the magnetic effect is so great, as not only to divide the stream, but to make it descend on each side of the ignited wick, producing a form resembling that of the letter W; and at the same time the top of the burning wick is greatly brightened by the stream of air that is impelled downwards upon it. In these experiments the magnetic poles should be about 0·25 of an inch apart.

A burning piece of amadou, or the end of a splinter of wood, produced the same effect.

By means of a small spark and stream of smoke, I have even rendered the power of an ordinary magnet, in affecting them, evident. The magnet was a good one, and the poles were close to each other and conical in form.

Before leaving this description of the general phænomenon and proceeding to a consideration of the principles of magnetic action concerned in it, I may say that a single pole of the magnet produces similar effects upon flame and smoke, but that they are much less striking and observable.

Though the effect be so manifest in a flame, it is not, at first sight, evident what is the chief cause or causes of the result. The *heat* of the flame is the most apparent and probable condition; but there are other circumstances which may be equally or more influential. Chemical action is going on at the time:—solid matter, which is known to be diamagnetic, exists in several of the flames used: and a great difference exists between the matter of the flame and the surrounding air. Now any or all of these circumstances of temperature, chemical action, solidity of part of the matter, and differential composition in respect to the surrounding air, may concur in producing or influencing the result.

I placed the wires of an electrometer, and also of a galvanometer, in various parts of the affected flame, but could not procure any indications of the evolution of electricity by any action on the instruments.

I examined the neighbourhood of the axial line as to the existence of any current in the air when there was no flame or heat there, using the visible fumes produced when little pellets of paper dipped in strong solutions of ammonia and muriatic acid were held near each other; and though I found that a stream of such smoke was feebly affected by the magnetic power, yet I was satisfied there was no current or motion in the common air, as such, between the poles. The smoke itself was feebly diamagnetic; due, I believe, to the solid particles in it.

But when flame or a glowing taper is used, strong currents are, under favourable circumstances, produced in the air. If the flame be between the poles, these currents take their course along the surface of the poles, which they leave at the opposite faces connected by the axial line, and passing parallel to the axial line, impinge on the opposite sides of the flame; and feeding the flame, they make part of it, and proceed out equatorially. If the flame be driven asunder by the force of these currents and retreat, the currents follow it; and so, when the flame is forked, the air which is between the poles forms a current which sets from the poles downwards and sideways towards the flame. I do not mean that the air in *every* case travels along the surface of the poles or along the axial lines, or even from between the poles; for in the case of the glowing taper, held half an inch or so beneath the axial line, it is the cool air which is next nearest to the taper, and (generally) between the taper and the axial line, that falls with most force upon it. In fact the movements of the parts of the air and flame are due to a differential action. We shall see presently that the air is diamagnetic as well as flame or hot smoke; *i. e.* that both tend, according to the general law which I have expressed in the Experimental Researches (2267, &c.), to move from stronger to weaker places of magnetic force, but that hot air and flame are more so than cold or cooler air: so, when flame and air, or air at different temperatures, exist at the same time within a space under the influence of magnetic forces, differing in intensity of action, the hotter particles will tend to pass from stronger to weaker places of action, to be replaced by the colder particles; the former therefore will have the effect of being repelled; and the currents that are set up are produced by this action, combined with the mechanical force or current possessed by the flame in its ordinary relation to the atmosphere.

It will be evident to you that I have considered flame only as a particular case of a general law. It is a most important and beautiful one, and it has given us the discovery of diamagnetism in gaseous bodies: but it is a complicated one, as I shall now proceed to show, by analysing some of its conditions and separating their effects.

For the purpose of examining the effect of heat alone in conducting to the diamagnetic condition of flame, a small helix of fine platina wire was attached to two stronger wires of copper, so that the helix could be placed in any given position as regarded the magnetic poles, and at the same time be ignited at pleasure by a voltaic battery. In this manner it was substituted for the burning taper, and gave a beautiful highly-heated current of air, unchanged in its chemical condition. When the helix was placed directly under the axial line, the hot air rose up between the poles freely, being rendered evident above by a thermometer, or by burning the finger, or even scorching paper; but as soon as the magnet was rendered active, the hot air divided into a double stream, and was found ascending on the two sides of the axial line; but a descending current was formed between the poles, flowing downwards towards the helix and the hot air, which rose and passed off sideways from it.

It is therefore perfectly manifest that hot air is diamagnetic in relation to, or more diamagnetic than, cold air; and, from this fact I concluded, that, by cooling the air below the natural temperature, I should cause it to approach the magnetic axis, or appear to be magnetic in relation to ordinary air. I had a little apparatus made, in which a vertical tube delivering air was passed through a vessel containing a frigorific mixture; the latter being so clothed with flannel that the external air should not be cooled, and so invade the whole of the magnetic field. The central current of cold air was directed downwards a little on one side of the axial line, and falling into a tube containing a delicate air-thermometer, there showed its effect. On rendering the magnet active, this effect however ceased, and the thermometer rose; but on bringing the latter under the axial line it again fell, showing that the cold current of air had been drawn inwards or attracted towards the axial line, *i. e.* had been rendered magnetic in relation to air at common temperatures, or less diamagnetic than it. The lower temperature was  $0^{\circ}$  F. The effect was but small; still it was distinct.

The effect of heat upon air, in so greatly increasing its diamagnetic condition, is very remarkable. It is not, I think, at all probable that the mere effect of expanding the air is the cause of the change in its condition, because one would be led

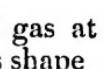
to expect that a certain bulk of expanded air would be less sensible in its diamagnetic effects than an equal bulk of denser air; just as one would anticipate that a vacuum would present no magnetic or diamagnetic effects whatever, but be at the zero point between the two classes of bodies (*Experimental Researches*, 2423, 2424). It is certainly true, that if the air were a body belonging to the magnetic class, then its expansion, being equivalent to dilution, would make it seem diamagnetic in relation to ordinary air (*Experimental Researches*, 2367, 2438); but that, I think, is not likely to be the case, as will be seen by the results described further on in reference to oxygen and nitrogen.

If the power conferred by heat is a direct consequence, and proportionate to the temperature, then it gives a very remarkable character to gases and vapours, which, as we shall see hereafter, possess it in common. In my former experiments (*Experimental Researches*, 2359, 2397) I heated various diamagnetic bodies, but could not perceive that their degree of magnetic force was at all increased or affected by the temperature given to them. I have again submitted small cylinders of copper and silver to the action of a single pole, at common temperatures and at a red heat, with the same result. If there was any effect of increased temperature, it was that of a very slight increase in the diamagnetic force, but I am not sure of the result. At present, therefore, the gaseous and vaporous bodies seem to be strikingly distinguished by the powerful effect which heat has in increasing their diamagnetic condition.

As all the experiments, whether on flame, smoke, or air, seemed to show that air had a distinct magnetic relation, which, though highly affected by temperature, still belonged to it at all temperatures; so it was a probable conclusion that other gaseous or vaporous bodies would be diamagnetic or magnetic, and that they would differ from each other even at common or equal temperatures. I proceeded therefore to examine them, delivering streams of each into the air, in the first instance, by fit apparatus and arrangements, and examining the course taken by these streams in passing across the magnetic field, the magnetic force being either induced or not at the time.

In delivering the various streams, I sometimes introduced the gases into a globe with a mouth and also a tubular spout, and then poured the gas out of the spout, upwards or downwards, according as it was lighter or heavier than air. At other times, as with muriatic acid or ammonia, I delivered the streams from the mouth of the retort. But as it is very im-

portant not to deluge the magnetic field with a quantity of invisible gas, I devised the following arrangement, which answered well for all the gases not soluble in water. A Woulf's bottle was chosen having three apertures at the top, *a*, *b* and *c*; a wide tube was fixed into aperture *a*, descending within the bottle to the bottom, and being open above and below; by this any water could be poured into the bottle and employed to displace the gas previously within it. Aperture *b* was closed by a stopper. Aperture *c* had an external tube, with a stop-cock fixed in it to conduct the gas to any place desired. To expel the gas and send it forward, a cistern of water was placed above the bottle, and its cock so plugged by a splinter of wood, that when full open it delivered only twelve cubic inches of fluid in a minute. This stream of water being directed into aperture *a*, and the cock of tube *c* open, twelve cubic inches of any gas within the Woulf's bottle was delivered in a minute of time; and this I found an excellent proportion for our magnet and apparatus.

With respect to the delivery of this gas at the magnetic poles, a piece of glass tube bent into this shape  was held by a clamp on the stage of the magnet, so that it could easily be slipped backward and forward, or to one side, and so its vertical part be placed anywhere below the axial line. The aperture at this end was about the one-eighth of an inch internal diameter. In the horizontal part near the angle was placed a piece of bibulous paper, moistened with strong solution of muriatic acid (when necessary). The horizontal part of the tube was connected and disconnected in a moment, when necessary, with the tube *c* of the gas-bottle, by a short piece of vulcanized rubber tube. If the gas to be employed as a stream were heavier than the surrounding medium, then the glass tube, instead of having the form delineated above, was so bent as to deliver its stream downwards and over the axial line. In this manner currents of different gases could be delivered, perfectly steady and under perfect command.

The next point was to detect and trace the course of these streams. A little ammonia vapour, delivered near the magnetic field, did this in some degree, but was not satisfactory; for, in the first place, the little cloud of muriate of ammonia particles formed, is itself diamagnetic; and further, the tranquil condition of the air in the magnetic field was then too much disturbed. Catch-tubes were therefore arranged, consisting of tubes of thin glass about the size and length of a finger, open at both ends, and fixed upon little stands so that they could be adjusted either over or under the magnetic poles at pleasure. When they were over the poles, I generally had

three at once; one over the axial line and one at each side. When they were under the poles, the lower end was turned up a little for the purpose of facilitating observation there.

The gas delivered at the poles, as already described, contained a little muriatic acid (obtained from the solution in the paper), but not enough to render it visible. To make it manifest up which catch-tube it passed, a little piece of bibulous paper, folded and bound round and suspended by a copper wire, was dipped in the solution of ammonia and hung in each of the tubes. It was then evident at once, by the visible fume formed at the top of one of the tubes, whether the gas delivered below passed up the one or the other tube, and which: and yet the gas was perfectly clear and transparent as it passed by the place of magnetic action.

In addition to these arrangements, I built up a sheltering chamber about the magnetic poles and field, to preserve the air undisturbed. This was about six inches long by four inches in width and height, and was easily made of thin plates of mica, which were put together or taken down in a moment. The chamber was frequently left more or less open at the top or bottom for the escape of gases, or the place of the catch-tubes. Its advantages were very great.

*Air.*—In the first place air was sent in under these arrangements, the stream being directed by the axial line. It made itself visible in the catch-tube above by the smoke produced; but whether the magnet was active or not, its course was the same; showing that, so far, the apparatus worked well, and did not of itself cause any erroneous indications.

*Nitrogen.*—This gas was sent from below upwards, and passed directly by the axial line into the catch-tube above; but when the magnet was made active, the stream was affected, and though not stopped in the middle catch-tube, part appeared in the side tubes. The jet was then arranged a little on one side of the axial line, so that, without the magnetic action, it still ascended and went up the middle catch-tube: then, when the magnetic action was brought on, it was clearly affected, and a great portion of it was sent to the side catch-tube. The nitrogen was, in fact, manifestly diamagnetic in relation to common air, when both were at the same temperature; but as four-fifths of the atmosphere consists of nitrogen, it seemed very evident, from the result, that nitrogen and oxygen must be very different from each other in their magnetic relations.

*Oxygen.*—A stream of oxygen was sent down through air between the poles. When there was no magnetic action it descended vertically, and when the magnetic action was on it

appeared to do the same; at all events it did not pass off equatorially. But as there was reason, from the above experiments with nitrogen, to expect that oxygen would appear, not diamagnetic but magnetic in air; so the place of the stream was changed and made to be on one side of the axial line. In this case it fell perfectly well at first into a catch-tube placed beneath; but as soon as the magnet was rendered active, the stream was deflected, being drawn towards the axial line, and fell into another catch-tube placed there to receive it. So oxygen appears to be magnetic in common air. Whether it be really so, or only less diamagnetic than air (a mixture of oxygen and nitrogen), we shall be better able to consider hereafter.

*Hydrogen.*—This gas proved to be clearly and even strongly diamagnetic; for notwithstanding the powerful ascensive force which its stream has in the atmosphere, because of its small specific gravity, still it was well deflected and sent equatorially. Considering the lightness of the gas, one might have expected that it would have been drawn towards the axial line, as a stream of rarefied air (if it could exist) would be. Its diamagnetic state, therefore, shows in a striking point of view, that gases, like solids, have peculiar and distinctive degrees of diamagnetic force.

*Carbonic acid.*—This gas made a beautiful experiment. The stream was delivered downwards a little on one side of the axial line; a catch-tube was placed a little further out, so that the stream should fall clear of it as long as there was no activity in the magnet. But on rendering the magnet efficient, the stream left its vertical direction, passed equatorially, and fell into the catch-tube; and by looking horizontally, could be seen flowing out at its lower extremity like a spring, and falling away through the air. Again, the magnet was thrown out of action, and a glass with lime-water placed beneath the lower end of the catch-tube; no carbonic acid appeared there, though the fluid in the glass was continually stirred; but the instant the magnet was made, the carbonic acid appeared in the catch-tube, fell into the glass and made the lime-water turbid. This gas therefore is diamagnetic in air.

*Carbonic oxide.*—This gas was carefully freed from carbonic acid before it was used. It was employed as a descending stream, and was apparently very diamagnetic: but it is to be remarked, that a substance which is so nearly the specific gravity of atmospheric air is easily dispersed right and left in it, and therefore that the facility of dispersion is not a correct indication of the diamagnetic force. By introducing a little ammonia into the mica chamber, it was, however, easily seen

that carbonic oxide was driven away equatorially with considerable power; and I judge from the appearance, that it is more diamagnetic than carbonic acid.

*Nitrous oxide.*—This gas was moderately, but clearly, diamagnetic in air. Much interest belongs to this and the other compounds of nitrogen and oxygen, both because they contain the same elements as air, and because of the relations of nitrogen and oxygen separately.

*Nitric oxide.*—I tried this gas both as an up and down current, but could not determine its magnetic condition. What with the action of the oxygen of the air, the change of the nature of the substances, and the heat produced, there was so much incidental disturbance and so little effect due to magnetic influence, that I could not be sure of the result. On the whole it was very slightly diamagnetic; but so little, that the effect might be due to the smoke particles which served to render it visible.

*Nitrous acid gas.*—Difficult to observe, but I believe it is slightly magnetic in relation to air.

*Olefiant gas* was diamagnetic, and well so. The little difference in specific gravity of this gas and air, even creates a difficulty in following the course of the olefiant gas, unless it be watched for on every side.

*Coal-gas.*—The coal-gas of London is lighter than air, being only about two-thirds in weight of the latter. It is very well diamagnetic, and gives exceedingly good and distinct results.

*Sulphurous acid gas* is diamagnetic in air. It was generated in a small tube containing liquid sulphurous acid; this being connected, in place of the gas bottle, with the delivery-tube and mouthpiece by the vulcanized rubber tube. The presence or absence of the gas in the catch-tube was well shown by ammonia, and still better by litmus paper.

*Muriatic acid.*—The retort in which it was generated was connected, as just described, with the delivery-tube. The gas was very decidedly diamagnetic in air.

*Hydriodic acid* was also diamagnetic in air. When there was an abundant stream of gas, its entrance into and passage through the side catch-tube, on rendering the magnet active, was very striking. When there was less gas, the stream was dispersed equatorially in all directions, and less entered the tube.

*Fluo-silicon.*—Diamagnetic in air.

*Ammonia.*—This gas was evolved from materials in a retort, and tested in the catch-tube above by muriatic acid in the paper. It was well diamagnetic, corresponding in this respect

with the character of its elements. It could also be very well indicated by reddened litmus paper held over the tubes.

*Chlorine* was sent from the Woulf's bottle apparatus, and proved to be decidedly diamagnetic in air. Either ammonia by its fumes, or litmus paper by its becoming bleached, served to indicate the entrance of the chlorine into the side catch-tube every time the magnet was rendered active.

*Iodine*.—A piece of glass tube was so shaped at its lower extremity as to form a chamber for the reception of iodine, which chamber had a prolonged mouth directed downwards so as to deliver the vapour formed within. On putting a little iodine into the chamber, then heating it, and especially the mouth part, by a spirit-lamp, and afterwards inclining the apparatus, abundance of the vapour of iodine was generated as the substance flowed on to the hotter parts, and passed in a good stream from the mouth downwards. This purple stream was diamagnetic in air, and could be seen flowing right and left from the axial line, when not too dense. If very dense and heavy, its gravity was such as to make it break through the axial line, notwithstanding the action of the magnet; still it was manifest that iodine is diamagnetic to air.

*Bromine*.—A little bromine was put into the horizontal part of the delivery tube, and then air passed over it by the apparatus already described. So much bromine rose into vapour as to make the air of a yellow colour, and caused it to fall well in a stream by the axial line. A little ammonia delivered near the magnetic field showed that this stream was diamagnetic, and hence it may fairly be presumed that the pure vapour of bromine would be diamagnetic also.

*Cyanogen*.—Strongly diamagnetic in air.

Taking air as the standard of comparison, it is very striking to observe, that much as gases appear to differ one from another in the degree of their diamagnetic condition, there are very few that are not more diamagnetic than it; and when the investigation is carried forward into the relation of the two chief constituents of air, oxygen and nitrogen, it is still more striking to observe the very low condition of oxygen, which, in fact, is the cause of the comparatively low condition of air. Of all the vapours and gases yet tried, oxygen seems to be that which has the least diamagnetic force. It is as yet a question where it stands; for it may be as low as a vacuum, or may even pass to the magnetic side of it, and experiment does not as yet give an answer to the question. I believe it to be diamagnetic; and this belief is strengthened by the action of heat upon it, to be described hereafter; but it is exceedingly low in the scale, and far below chlorine, iodine, and such like bodies.

All the compounds of oxygen and nitrogen seem to show the influence of the presence of the oxygen. Nitrous acid seems to be less diamagnetic than air. Nitric oxide mingled with nitrous acid and warm, is about as air. Nitrous oxide is clearly diamagnetic in air, though it contains more oxygen: but it also contains more nitrogen than air, and is also denser than it, so that there is more matter present; still I think the results are in favour of the idea that oxygen is diamagnetic. By referring to the relation of carbonic oxide to carbonic acid, described further on, it will be seen that the addition of oxygen seems to make a body less diamagnetic. But the truth may be, not that oxygen is really magnetic, but that a compound body possesses a specific diamagnetic force, which is not the sum of the forces of its particles.

It is very difficult to form more than a mere guess at the relative degree of diamagnetic force possessed by different gaseous bodies when they are examined only in air, because of the many circumstances which tend to confuse the results. First, there is the invisibility of the gas which deprives one of the power of adjusting by sight so as to obtain the best effect: then, there is the difference of gravity; for if a gas ascend or descend in a rapid stream, it may seem less deflected than another flowing more slowly, though it be more diamagnetic; and as to gases nearly of the specific gravity of air, whether more or less diamagnetic, they are almost entirely dispersed in different directions, so that little only enters the catch-tube. Another modifying circumstance is the distance of the aperture delivering gas from the axial line, which, to obtain the maximum effect, ought to vary with the gravity of the gases and their diamagnetic force. Again, it is important that the magnetic field be not filled with the gas to be examined, and that generally speaking only a moderate stream be employed; which however must depend again upon the specific gravity.

The only correct way therefore of comparing two gases together is to experiment with them one in the other. For the experiments made with gases, in gases or in air are differential, and similar in their nature with those made on a former occasion with solutions (*Experimental Researches*, 2362, &c.) ; I therefore changed the surrounding medium in a few experiments, substituting other gases for air; and first chose carbonic acid as a body easy to experiment with, and one that would, probably, be more powerfully than some other of the gases, diamagnetic (I speak as to the appearances or relative results only) in air.

I constructed a kind of tray or box, by folding up a doubled sheet of waxed paper; thus making a vessel thirteen inches

long, five inches wide, and five inches high. This was placed on the ends of the great magnet, and the terminal pieces of iron before described, placed in it. The box was covered over loosely by plates of mica, and formed a long square chamber in which were contained the magnetic poles and field. All the former arrangements in respect of the magnetic field, the delivery-tube, the catch-tubes, &c., were then made; and, lastly, the box was filled with carbonic acid by a tube, which entered it at one corner; and was, from time to time, supplied with a fresh portion of gas, as the previous contents became diluted with gases or air. Everything answered perfectly, and the following results were easily obtained.

*Air* passed axially, being less diamagnetic than carbonic acid gas.

*Oxygen* passed to the magnetic axis, as was to be expected.

*Nitrogen* went equatorially, being therefore diamagnetic, even in carbonic acid.

*Hydrogen*, *coal-gas*, *olefiant gas*, *muriatic acid* and *ammonia* passed equatorially in carbonic acid, and were fairly diamagnetic in relation to it.

*Carbonic oxide* was very fairly diamagnetic in carbonic acid gas. Here the effect of oxygen seems to be very well illustrated. Equal volumes of carbonic oxide and carbonic acid contain equal quantities of carbon; but the former contains only half as much oxygen as the latter. Yet it is more diamagnetic than the latter; so, that, though an additional volume and quantity of oxygen, equal to that in the carbonic oxide, is in the carbonic acid added and compressed into it, it does not add to, but actually takes from, the diamagnetic force.

*Nitrous oxide* appears to be slightly diamagnetic in relation to carbonic acid; but nitric oxide gas was in the contrary relation and passed towards the axial line.

Hence it seems that carbonic acid, though more diamagnetic than air, is not far removed from it in that respect; and this position it probably holds because of the quantity of oxygen in it. The apparent place of nitrous oxide close to it appears, in a great measure, to depend on the same circumstance of oxygen entering largely into its composition. Still it is manifest that the action is not *directly* as the oxygen, for then common air would be more diamagnetic than either of them. It seems rather that the forces are modified, as in the case also of iron and oxygen, and that each compound body has its peculiar but constant intensity of action.

In order to make similar experiments in light gases, the two terminal pieces of the magnet were raised, so that they might be covered by a French glass shade, which, with its

stand, made a very good chamber about them. The pipe to supply and change the gaseous medium, and also that for bringing the gas under trial as a stream into the magnetic field, passed through holes made in the bottom of the stand. The different gases to be compared with those employed as media, were, except in the cases of ammonia and chlorine, mingled with a trace of muriatic acid, as before described. The gaseous media used were two, coal-gas and hydrogen. Whilst using coal-gas, I observed the direction of the currents of the other gases in it by bringing a little piece of paper, at the end of a wire and dipped in ammonia solution, near the stream. In the case of the hydrogen, I diffused a little ammonia through the whole of the gas in the first instance.

*Air* passed towards the axial line in coal-gas, but was not much affected.

Oxygen had the appearance of being strongly magnetic in coal-gas, passing with great impetuosity to the magnetic axis, and clinging about it; and if much muriate of ammonia fume were purposely formed at the time, it was carried by the oxygen to the magnetic field with such force as to hide the ends of the magnetic poles. If then the magnetic action were suspended for a moment, this cloud descended by its gravity; but being quite below the poles, if the magnet were again rendered active, the oxygen cloud immediately started up and took its former place. The attraction of iron filings to a magnetic pole is not more striking than the appearance presented by the oxygen under these circumstances.

*Nitrogen*.—Clearly diamagnetic in coal-gas.

*Olefiant*, *carbonic oxide*, and *carbonic acid* gases were all slightly, but more or less diamagnetic in the coal-gas.

On substituting hydrogen as the surrounding medium in place of coal-gas, more care was taken in the experiments. Each gas experimented upon was tried in it twice at least; first in the hydrogen of a previous experiment, and then in a new atmosphere of hydrogen.

*Air*.—Air passes axially in hydrogen when there is very little smoke in it: when there is much smoke in the stream the latter is either indifferent or tends to pass equatorially. I believe that air and hydrogen cannot be far from each other.

*Nitrogen* is strikingly diamagnetic in hydrogen.

*Oxygen* is as strikingly magnetic in relation to hydrogen. It presented the appearances already described as occurring in coal-gas; but as the jet delivered the descending stream of oxygen a little on one side of the axial line, its centrifugal power, in relation to the axial line, was so balanced by the centripetal power produced by the magnetic action, that the

stream at first revolved in a regular ring round the axial line, and produced a cloud that continued to spin round it as long as the magnetic force was continued, but fell down to the bottom of the chamber when that force was removed.

*Nitrous oxide*.—This gas was clearly diamagnetic in the hydrogen, and gave rise to a very beautiful result in consequence of its following the oxygen; for at the beginning of the experiment, the little oxygen contained in the conducting tube passed axially; but the instant that was expelled, and the nitrous oxide issued forth, the stream changed its direction, and passed off diamagnetically in the most striking manner.

*Nitric oxide*.—This gas passed equally in hydrogen, and therefore is magnetic in relation to it.

*Ammonia*.—Diamagnetic in hydrogen.

*Carbonic oxide, carbonic acid, and olefiant gases* were diamagnetic in hydrogen; the last most so, and the carbonic acid apparently the least.

*Chlorine* was slightly diamagnetic in hydrogen. It was clearly so; but the cloudy particles might conduce much to the small effect produced.

*Muriatic acid gas*.—I think it was a little diamagnetic in the hydrogen.

Notwithstanding the many disturbing causes which interfere with first and hasty experiments of this kind, and produce results which occasionally cross and contradict each other, still there are some very striking considerations which arise in comparing the gases with each other at the same temperature. Foremost amongst these is the place of oxygen; for of all the gaseous bodies yet tried it is the least diamagnetic, and seems in this respect to stand far apart from the rest of them. The condition of nitrogen, as being highly diamagnetic, is also important. The place of hydrogen, as being less diamagnetic than nitrogen, and of chlorine, which, instead of approaching to oxygen, is above hydrogen, and also of iodine, which is probably far above chlorine, are marked circumstances.

Air of course owes its place to the proportion and the individual diamagnetic character of the oxygen and nitrogen in it. The great difference existing between these two bodies in respect of magnetic relation, and the striking effect presented by oxygen in coal-gas and hydrogen, bodies not far removed from nitrogen in diamagnetic force, made me think it might not be impossible to separate air into its two chief constituents by magnetic force alone. I made an experiment for this purpose but did not succeed; but I am not convinced that it cannot be done. For since we can actually distinguish certain gases, and especially these by their magnetic properties, it does not

seem impossible that sufficient power might cause their separation from a state of mixture.

In the course of these experiments I subjected several of the gases to heat, to ascertain whether they generally underwent the same exaltation of their diamagnetic power which occurred with common air. For this purpose a helix of platina wire was placed in the mouth of the delivering tube, which itself was placed below the magnetic axis between the poles. The helix could be raised to any temperature by a little voltaic battery, and any gas could be sent through it and upwards across the magnetic field by means of the Woulf's bottle apparatus already described. It was easy to ascertain whether the gas went directly up between the poles, or, on making the magnet, left that direction and formed two equatorial side-streams, either by the sensation on the finger, or by a spiral thermoscope formed of a compound lamina of platinum and silver placed in a tube above. In every case the hot gas was diamagnetic in the air, and I think far more so than if the gas had been at common temperatures. The gases tried were as follows: oxygen, nitrogen, hydrogen, nitrous oxide, carbonic acid, muriatic acid, ammonia, coal-gas, olefiant gas.

But as in these experiments the surrounding air would, of necessity, mingle with the gas first heated, and so form, in fact, a part of the heated stream, I arranged the platinum helix so that I could heat it in a given gas, and thus compare the same gas at different temperatures with itself.

A stream of hot oxygen in cold oxygen was powerfully diamagnetic. The effect and its degree may be judged of by the following circumstances. When the platinum helix below the axial line was ignited, the effect of heat on the indicating compound spiral, placed in a tube over the axial line, was such as to cause its lower extremity to pass through one and a half revolutions, or  $540^\circ$ : when the magnetic force was rendered active, the spiral returned through all these degrees to its first position, as if the ignited helix below had been lowered to the common temperature or taken away; and, yet in respect of it, nothing had been changed. On rendering the magnet inactive, the current of hot oxygen instantly resumed its perpendicular course and affected the thermoscope as before.

On experimenting with carbonic acid, it was found that hot carbonic acid was diamagnetic to cold carbonic acid; and the effects were apparently as great in amount as in oxygen.

On making the same arrangement in hydrogen, I failed to obtain any result regarding the relation of the hot and cold gas, for this reason:—that I could not, in any case, either

with or without the magnetic action, obtain any signs of heat on the thermoscopic spiral above, even when the platinum helix, not more than an inch below it, was nearly white hot. This effect is, I think, greatly dependent upon the rapidity with which hydrogen is heated and cooled in comparison with other gases, and also upon the vicinity of the cold masses of iron forming the magnetic poles, between which the hot gas has to pass in its way upwards : and it is most probably connected with the fact observed by Mr. Grove of the difficulty of igniting a platinum wire in hydrogen.

When the igniting helix was placed in coal-gas, it was found that the hot gas was diamagnetic to that which was cold; as in all the other cases. Here, again, an effect like that which was observed in hydrogen occurred ; for when there was no magnetic action, the ascending stream of hot coal-gas could cause the thermoscopic spiral to revolve through only  $280^{\circ}$  or  $300^{\circ}$ , in place of above  $540^{\circ}$ ; through which it could pass when the surrounding gas was oxygen, air, or carbonic acid ; and that even when the helix was at a higher temperature in the coal-gas than in any of these gases.

The proof is clear then that oxygen, carbonic acid, and coal-gas, are more diamagnetic hot than cold. The same is the case with air ; and as air consists of four-fifths nitrogen and only one-fifth oxygen, and yet shows an effect of this kind as strongly as oxygen, it is manifest that nitrogen also has the same relation when hot and cold.

Of the other gases also I have no doubt ; though to be quite certain, they ought to be tried in atmospheres of their own substance, or else in gases more diamagnetic at common temperatures than they. The olefiant and coal-gases in air easily bore the elevation of the helix to a full red heat, without inflaming when out of the exit-tube: the hydrogen required that the helix should be at a lower temperature. Muriatic acid and ammonia showed the division of the one stream into two, very beautifully, on holding blue and red litmus paper above.

There is another mode of observing the diamagnetic condition of flame, and experimenting with the various gases, which is sometimes useful, and should always be understood, lest it inadvertently might lead to confusion. I have a pair of terminal magnetic poles which are pierced in a horizontal direction, that a ray of light may pass through them. The opposed faces of these vertical poles are not, as in the former case, the rounded ends of cones ; but, though rounded at the edges, may be considered as flat over an extent of surface an inch in diameter. The pierced passages are in the form of cones, the truncation of which in this flat surface is rather

more than half an inch in diameter. When these poles were in their place, and from 0·3 to 0·4 of an inch apart, a taper flame, burning freely between them, was for a few moments unaffected by throwing the magnet into action; but then it suddenly changed its form, and extending itself axially, threw off two horizontal tongues, which entered the passages in the poles; and thus it continued as long as the magnetism continued, and no part of it passed equatorially.

On using a large flame made with the cotton ball and æther, two arms could be thrown off from the flame by the force of the magnetism, which passed in an equatorial direction, as before; and other two parts entered the passages in the magnetic poles, and actually issued out occasionally at their further extremities.

When the poles were about 0·25 of an inch apart, and the smoking taper was placed in the middle between them level with the centres of the passages, the effect was very good; for the smoke passed axially and issued out at the further ends of the pole passages.

Coal-gas delivered in the same place also passed axially, *i. e.* into the pole passages and parallel to the line joining them.

A little consideration easily leads to the true cause of these effects, and shows that they are not inconsistent with the former results. The law of all these actions is, that if a particle, placed amongst other particles, be more diamagnetic (or less magnetic) than them, and free to move, it will go from strong to weaker places of magnetic action; also, that particles less diamagnetic will go from weaker to stronger places of action. Now with the poles just described, the line or lines of maximum force, are not coincident with the axis of the holes pierced in the poles, but lie in a circle having a diameter, probably, a little larger than the diameter of the holes; and the lines within that circle will be of lesser power, diminishing in force towards the centre. A hot particle therefore within that circle will be driven inwards, and, being urged by successive portions of matter driven also inwards, will find its way out at the other ends of the passages, and therefore seem to go in an axial direction; whilst a hot particle outside of that circle of lines of maximum force will be driven outwards, and so, with others, will form the two tongues of flame which pass off in the equatorial direction. By bringing the glowing taper to different parts, the circle of lines of maximum magnetic intensity can be very beautifully traced; and by placing the taper inside or outside of that circle, the smoke could be made to pass axially or equatorially at pleasure.

I arranged an apparatus on this principle for trying the  
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gases, but did not find it better than, or so good as, the one I have described.

Such are the results I have obtained in verifying and extending the discovery made by P. Bancalari. I would have pursued them much further, but my present state of health will not permit it: I therefore send them to you with, probably, many imperfections. It is now almost proved that many gaseous bodies are diamagnetic in their relations, and probably all will be found to be so. I say almost proved; for it is not, as yet, proved in fact. That many, and most, gaseous bodies are subject to magnetic force is proved; but the zero is not yet distinguished. Now, until it is distinguished, we cannot tell which gaseous bodies will rank as diamagnetic and which as magnetic; and, also, whether there may not be some standing at zero. There is evidently no natural impossibility to some gases or vapours being magnetic, or that some should be neither magnetic nor diamagnetic. It is the province of experiment to decide such points; and the affirmative or negative may not be asserted before such proof is given, though it may, very philosophically, be believed.

For myself I have always believed that the zero was represented by a vacuum, and that no body really stood with it. But though I have only guarded myself from asserting more than I knew, Zantedeschi (and I think also De la Rive), with some others, seem to think that I have asserted the gases are *not* subject to magnetic action; whereas I only wished to say that I could not find that they were, and perhaps were not: I will therefore quote a few of my words from the Experimental Researches. Speaking of the preparation of a liquid medium at zero, I say, "Thus a *fluid* medium was obtained, which practically, as far as I could perceive, had every magnetic character and effect of a gas, *and even of a vacuum*, &c."—Experimental Researches, 2423. Again, at (2433) I say, "At one time I looked to air and gases as the bodies which allowing attenuation of their substance without addition, would permit of the observation of corresponding variations in their magnetic properties, but now all such power by rarefaction *appears* to be taken away." And further down at (2435), "Whether the negative results obtained by the use of gases and vapours depend upon the *smaller quantity of matter* in a given volume, or whether they are the direct consequences of the altered physical condition of the substance, is a point of very great importance to the theory of magnetism. I have imagined in elucidation of the subject an experiment, &c., but expect to find great difficulty in carrying it into execution, &c." Happily P. Bancalari's discovery has now settled this matter

for us in a most satisfactory manner. But where the true zero is, or that every body is more or less removed from it on one side or the other, is not, as yet, experimentally shown or proved.

I cannot conclude this letter without expressing a hope that since gases are shown to be magnetically affected, they will also shortly be found, when under magnetic influence, to have the power of affecting light (Experimental Researches, 2186, 2212). Neither can I refrain from signalizing the very remarkable and direct relation between the forces of heat and magnetism which is presented in the experiments on flame, and heated air and gases. I did not find on a former occasion (Experimental Researches, 2397) that solid diamagnetic bodies were sensibly affected by heat, but shall repeat the experiments and make more extensive ones, if the Italian philosophers have not already done so. In reference to the effect upon the diamagnetic gases, it may be observed that, speaking generally, it is in the same direction as that of heat upon iron, nickel and cobalt; *i. e.* heat tends in the two sets of cases, either to the diminution of magnetic force, or the increase of diamagnetic force; but the results are too few to allow of any general conclusion as yet.

As air at different temperatures has different diamagnetic relations, and as the atmosphere is at different temperatures in the upper and lower strata, such conditions may have some general influence and effect upon its final motion and action, subject as it is continually to the magnetic influence of the earth.

I have for the sake of brevity frequently spoken in this letter of bodies as being magnetic or diamagnetic in relation one to another, but I trust that in all the cases no mistake of my meaning could arise from such use of the terms, or any vague notion arise respecting the clear distinction between the two classes, especially as my view of the true zero has been given only a page or two back.

I am, my dear Sir,

Yours, &c.,

*Richard Taylor, Esq.,  
Ed. Phil. Mag., &c. &c.*

M. FARADAY.

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LXV. *On the Motions presented by Flame when under the  
Electro-Magnetic Influence.* By Prof. ZANTEDESCHI.

THE most eminent philosophers have at all times maintained the universality of the magnetism of bodies\*; and in our days Faraday is the only one who has placed the expansi-

\* *Raccolta Fisico-Chimica Italiana*, t. iii. Dei corpi magnetici e diamagnetici.

ble fluids at the zero of the scale of action among magnetic and diamagnetic bodies. On the 21st of September 1847, at the Physical Section of the Ninth Italian Scientific Congress in Venice, Padre Bancalari, Professor of Physics in the Royal University of Genoa, read a memoir on the universality of magnetism; and the argument was considered by philosophers to be of such importance, that a desire arose to verify chiefly the action of magnetism on expansible fluids. It was announced by the Reporter Belli at the sitting of the 27th of September, that it had been proved in the presence of various philosophers that, on the interposition of a flame between the two poles of an electro-magnet, it was repulsed at the instant the electric current was closed, to return to the first position the instant it was broken. This discovery received well-merited applause in the sitting of the 28th of September, from the General Secretary and the Secretary of the Section of Physics. A wish was expressed by some to witness the experiment of Bancalari; and a Daniell's apparatus having been got ready, of ten elements eighteen centimetres each in dimension, I endeavoured to repeat the experiment in the Cabinet of Physics of the Royal Imperial Lyceum of Venice; but I did not chance to see the asserted phænomenon. My temporary magnet had the power of sustaining above 48 kilogrms. weight; but as my principle is, that a negative argument never destroys a positive one, I for my further information requested the machinist Cobres to give me the particulars of the apparatus; Belli not having treated of these in his report, and they having escaped Prof. Zambra, the Secretary of the Section. I knew that the two pieces of soft iron, which constituted the interrupted anchor, were perforated in the axial direction. I suspected that the repulsion of the flame was not the immediate effect of the magnetism, but of two currents of air issuing from the apertures of the perforated keeper generated by a vorticose movement produced by the magnetism, as the celebrated Faraday had observed in liquids\*; and I was confirmed in this suspicion by the negative experiment which I had instituted in Venice with solid pieces. On arriving in Turin, I communicated my doubts to the well-known mechanicians Jest, father and son, who to their professional abilities unite a rare courtesy. They soon furnished me in their laboratory with a Bunsen's apparatus, and constructed terminal pieces of soft iron forming the interrupted anchor, both solid and pierced, of a parallelepipedon and cylindric form, as I pointed out to them; and I have repeated the experiments in their company: the temporary

\* *Raccolta*, cited above, t. ii. Relazione dell' influenza delle forze elettriche e magnetiche sulla luce ed il calorico.

magnet, made in the shape of a horseshoe, was formed of a cylinder of soft iron of the length of 0<sup>m</sup>.335 and the diameter of 0<sup>m</sup>.015; and its electro-magnetic spiral was formed of a copper wire 33<sup>m</sup> long, and of a diameter of a millimetre and a third; the internal distance of the poles was 0<sup>m</sup>.027; the two solid parallelepipedon contacts, forming the interrupted anchor, were 0<sup>m</sup>.04 long; and of the sides 0<sup>m</sup>.011 and 0<sup>m</sup>.006: and the hollow terminal pieces were 0<sup>m</sup>.035 long; and of the side 0<sup>m</sup>.009. They were placed at a distance from one another of four to five millimetres, the magnet being kept in a vertical position with the poles turned upwards. In front of the interval of the separation of the contact pieces was placed the flame of a small candle, or of a little oil or alcohol lamp, so that it surmounted with its top by nearly a fourth the thickness of the contacts. The electric circuit was closed by copper wires, and the metallic unions were maintained both at the magnetic poles and at those of the pile by clamps: one of the wires therefore was divided into two equal parts, and the ends being dipped into a tumbler of mercury, allowed the closing and opening of the circuit at pleasure.

*I have constantly observed repulsion in the act of closing the circle, which lasted the whole time that the magnetism was kept up; and, when in the act of opening the circle, I saw the flame return to its primitive position.* Well-satisfied with having in this manner confirmed this important fact which reflects honour on its discoverer, I applied myself to the study of the phænomenon, and I found—

I. *That this happens with contacts of both solid and hollow soft iron; whereupon I abandoned my suspicion that the movement of the flame was attributable to currents of air; I convinced myself that it was an immediate action of the magnetism upon the flame,—a fact of the greatest importance to science.*

II. *That the repulsion, when it is quite distinct and the flame quite pure, and terminated in a well-shaped top, is accompanied by depression: repulsion and depression are simultaneously observed at the closing of the circle; the return of the flame and rising of the same, at the opening of the circle.*

III. *That, ceteris paribus, the greatest effect takes place when the flame is touching the convex of the magnetic curves indicated by iron filings.*

IV. *That the action is null, or almost null, when the flame is placed in the centre of the interval which separates the two contacts.*

V. *That in the manifestation of the effects stated above, it is not necessary for the contacts to be entirely separated: they may*

be placed at an angle and touch at two corners; the flame placed within the base of this triangle, generally manifests the two phænomena indicated.

VI. *That there is a certain mass of the contacts (or keeper pieces) which is the most efficacious: beyond a limit, which can be shown by experiment, increase of the mass causes a diminution of the effect:* from this I found the cause of my negative results, which I obtained in Venice in the first experiments that I made.

VII. *That the movements of the flame increase with the number of the pairs (of battery plates).* With one pair the effect was not perceptible to me\*: with two pairs the movements began to show themselves; with three pairs they became distinct, and increased with the increase of the number of pairs up to ten, which was the greatest that I employed in this experiment. The pairs were of the known ordinary size.

On the repetition of the phænomena as above stated, the precaution was taken to cover the apparatus with a bell, which was open above and supported by two discs below, which left a free access to the air, by which to support the combustion: in this manner all agitation and danger of disturbance under the circumstances were avoided.

I must not forget, in concluding this article, to state that the celebrated Prof. Gazzaniga, starting from his numerous experiments, which demonstrate the influence of magnetism upon the same aërifluid, in a manner therefore different from that of Bancalari, was induced to consider the sun and all the other celestial bodies as so many enormous magnets; by which he established that attraction is merely an effect of the magnetism of the great celestial masses placed at an enormous distance,—an idea which reappeared in 1846 in Prussia, and in 1847 in France, as we see from the *Comptes Rendus* of the Royal Academy of Sciences at Paris. The mystery that attraction operates at a distance without intermedia would be removed in this case, and the phænomena of attraction would enter again into the class of those of common dynamics.

Dalla Gazz. Piem., Oct. 12, 1847, No. 242.

\* Messrs. Jest prepared for me last evening an electro-magnet of a circular form interrupted by a prismatic section having an interval of two millimetres; and I had, without need of contact pieces, the phænomena distinct with a single element. The most conspicuous movements here appeared in the greater proximity of the flame to the section.

The complete apparatus, of a circular form, furnished with a glass bell with its accessories is sold in Turin by Messrs. Jest, at the price of thirty francs, not including the electro-motor.

LXVI. *On Asymptotic Straight Lines, Planes, Cones and Cylinders to Algebraical Surfaces.* By THOMAS WEDDLE\*.

**I**N the Cambridge Mathematical Journal, first series, vol. iv. pp. 42-47, the late D. F. Gregory gave a very excellent method of determining the asymptotes to algebraical curves. I here purpose considering the corresponding subject relative to algebraical surfaces; and as this seems to have as yet engaged but little attention (if any), I trust the discussion will not be unacceptable to the mathematical readers of this Journal.

*Definitions.*

1. A straight line which passes through a point at a finite distance and touches a surface at an infinite distance, is called an *asymptotic straight line*, or simply an *asymptote* to the surface.
2. If *every* straight line drawn in a plane be an asymptote to a surface, the plane is styled a **CONICAL asymptotic plane** to the surface.
3. If all straight lines drawn in a plane parallel to a straight line in that plane be asymptotes to a surface, the plane is denominated a **CYLINDRICAL asymptotic plane** to the surface.
4. An *asymptotic cone* or *cylinder* to a surface is a cone or cylinder having its generators asymptotes to the surface.

If  $\varphi_q(xyz)$  denote a homogeneous function of  $x, y, z$  of the  $q$ th degree, it is plain that a surface of the  $p$ th degree may be denoted thus:

$$\varphi_p(xyz) + \varphi_{p-1}(xyz) \dots + \varphi_1(xyz) + \varphi_0 = 0. \quad . \quad (1.)$$

Let

$$\frac{x-\alpha}{l} = \frac{y-\beta}{m} = \frac{z-\gamma}{n} = r \dagger \quad . \quad . \quad . \quad (2.)$$

be the equations of an asymptote to (1.) passing through the point  $(\alpha\beta\gamma)$ : hence

$$x = lr + \alpha, \quad y = mr + \beta, \quad \text{and} \quad z = nr + \gamma;$$

substitute these values of  $x, y$  and  $z$  in (1.) and develope each term, the result is,

\* Communicated by the Author.

† The axes may be either rectangular or oblique; only in the former case we shall have

$$l^2 + m^2 + n^2 = 1;$$

but in the latter,

$$l^2 + m^2 + n^2 + 2fmn + 2glm + 2hlm = 1,$$

$f, g, h$  denoting the cosines of the angles which the axes make with each other.

$$\left. \begin{aligned} & \varphi_p r^p + (D\varphi_p + \varphi_{p-1})r^{p-1} + \left( \frac{1}{2} D^2\varphi_p + D\varphi_{p-1} + \varphi_{p-2} \right) r^{p-2} \\ & \dots + \left( \frac{1}{2 \cdot 3 \dots s} D^s \varphi_p + \frac{1}{2 \cdot 3 \dots (s-1)} D^{s-1} \varphi_{p-1} + \dots \right. \\ & \left. \dots + D\varphi_{p-s+1} + \varphi_{p-s} \right) r^{p-s} \dots = 0^*, \end{aligned} \right\} \quad (3.)$$

where  $D$  denotes the operation

$$\alpha \frac{d}{dl} + \beta \frac{d}{dm} + \gamma \frac{d}{dn}.$$

This equation will determine the values of  $r$  at the points in which the straight line (2.) cuts the surface (1.); now for all lines parallel to an asymptote, one of these points is evidently at an infinite distance; hence a root of (3.) being infinite, we must have

$$\varphi_p = 0; \quad \dots \quad (4.)$$

and this equation determines the directions of the asymptotes. The equation (3.) hence becomes

$$\left. \begin{aligned} & (D\varphi_p + \varphi_{p-1})r^{p-1} + \left( \frac{1}{2} D^2\varphi_p + D\varphi_{p-1} + \varphi_{p-2} \right) r^{p-2} \dots \\ & + \left( \frac{1}{2 \cdot 3 \dots s} D^s \varphi_p + \frac{1}{2 \cdot 3 \dots (s-1)} D^{s-1} \varphi_{p-1} + \dots \right. \\ & \left. + D\varphi_{p-s+1} + \varphi_{p-s} \right) r^{p-s} + \dots = 0; \end{aligned} \right\} \quad (5.)$$

in which values of  $l, m, n$  satisfying (4.) must be substituted. Now an asymptote being a tangent at an infinite distance, it follows that the asymptote will be distinguished from all lines having the same direction by a root of (5.) being infinite; we must therefore have

$$D\varphi_p + \varphi_{p-1} = 0;$$

that is,

$$\frac{d\varphi_p}{dl} \alpha + \frac{d\varphi_p}{dm} \beta + \frac{d\varphi_p}{dn} \gamma + \varphi_{p-1} = 0. \quad \dots \quad (6.)$$

The equation (4.) shows that every asymptote is parallel to some generator or other of the cone

$$\varphi_p(xyz) = 0; \quad \dots \quad (7.)$$

\* In this paper I restrict  $\theta, \phi, \psi, \chi$  (either with or without a letter or figure subscripted) to denote homogeneous functions only; and when these symbols stand alone, they are to be understood as functions of  $l, m, n$ ; in other cases the symbols of quantity must be written; thus  $\chi_q(xyz)$  (a homogeneous function of  $x, y, z$  of the  $q$ th degree) means the same function of  $x, y, z$  that  $\chi_q$  does of  $l, m, n$ .

and since  $(\alpha, \beta, \gamma)$  may be any point in each asymptote, (6.) denotes the locus ( $\alpha, \beta, \gamma$  being the variable coordinates) of the asymptotes parallel to the same generator of (7.); this locus is therefore a cylindrical asymptotic plane, and it is parallel to that tangent plane of the cone (7.) which touches along the generator. Hence, to find the equation of a cylindrical asymptotic plane, we have only to take such values of  $l, m, n$  as satisfy (4.) and substitute them in (6.). It thus appears that when the cone (7.) is not imaginary, there is an indefinite number of cylindrical asymptotic planes; one indeed parallel to every tangent plane of the cone (7.), with a few exceptions, which I shall consider presently.

Should (4.), or, which is the same thing, (7.) be resolvable into factors, then (7.) will in reality denote as many conical surfaces; and if any of these factors be of the first degree, the corresponding conical surface will degenerate into a plane.

Let  $\theta_q$  be any factor of  $\phi_p$ , and put

$$\psi_{p-q} = \frac{\phi_p}{\theta_q};$$

hence (6.) becomes

$$\theta_q \cdot D\psi_{p-q} + \psi_{p-q} D\theta_q + \phi_{p-1} = 0,$$

when  $\theta_q = 0$ , this reduces to

$$\psi_{p-q} \left\{ \frac{d\theta_q}{dl} \alpha + \frac{d\theta_q}{dm} \beta + \frac{d\theta_q}{dn} \gamma \right\} + \phi_{p-1} = 0; \quad . \quad (8.)$$

and this equation, together with  $\theta_q = 0$ , will supply the place of (4.) and (6.) for those cylindrical asymptotic planes that are parallel to the tangent planes of the cone  $\theta_q(xyz) = 0$ . Also similar equations may be found for every factor of  $\phi_p$ .

If the equations

$$\phi_p = 0, \quad \frac{d\phi_p}{dl} = 0, \quad \frac{d\phi_p}{dm} = 0, \quad \frac{d\phi_p}{dn} = 0,$$

can be satisfied by simultaneous values  $(l_1, m_1, n_1)$  of  $l, m, n$ , (6.) cannot be satisfied unless  $\phi_{p-1}$  also = 0; if  $\phi_{p-1}$  should not = 0, there will be no cylindrical asymptotic plane corresponding to these values of  $l, m, n$ ; but if  $\phi_{p-1} = 0$ , so that we have

$$\phi_p = 0, \quad \frac{d\phi_p}{dl} = 0, \quad \frac{d\phi_p}{dm} = 0, \quad \frac{d\phi_p}{dn} = 0, \quad \phi_{p-1} = 0*, \quad (9.)$$

then (6.) will be satisfied independently of  $\alpha, \beta, \gamma$ . We have only to recur however to (5.), and equate to zero the coefficient

\* Since  $\phi_p$  is a homogeneous function of  $l, m, n$  of the  $p$ th degree, we have

$$p\phi_p = \frac{d\phi_p}{dl} l + \frac{d\phi_p}{dm} m + \frac{d\phi_p}{dn} n;$$

hence the equations (9.) amount only to four independent equations—the last four.

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of the first power of  $r$  that does not vanish independently of  
any relation among  $\alpha, \beta, \gamma$ . If this coefficient be that of  $r^{p-2}$ ,  
we have

$$\frac{1}{2} D^2 \varphi_p + D\varphi_{p-1} + \varphi_{p-2} = 0;$$

that is,

$$\left. \begin{aligned} & \frac{1}{2} \frac{d^2 \varphi_p}{dl^2} \alpha^2 + \frac{1}{2} \frac{d^2 \varphi_p}{dm^2} \beta^2 + \frac{1}{2} \frac{d^2 \varphi_p}{dn^2} \gamma^2 + \frac{d^2 \varphi_p}{dm \cdot dn} \beta \gamma + \frac{d^2 \varphi_p}{dl \cdot dn} \alpha \gamma \\ & + \frac{d^2 \varphi_p}{dl \cdot dm} \alpha \beta + \frac{d\varphi_{p-1}}{dl} \alpha + \frac{d\varphi_{p-1}}{dm} \beta + \frac{d\varphi_{p-1}}{dn} \gamma + \varphi_{p-2} = 0 \end{aligned} \right\} \quad (10.)$$

This equation denotes a surface which is evidently the locus of the asymptotes which are parallel to that generator of (7.) whose equations are  $\frac{x}{l_1} = \frac{y}{m_1} = \frac{z}{n_1}$ . Hence (10.) must denote a cylindrical surface; and as its generators are all asymptotes, it is an asymptotic cylinder of the second degree (which may in certain cases degenerate into one or two cylindrical asymptotic planes). Should the values of  $l, m, n$  satisfying (9.) also cause  $\alpha, \beta, \gamma$  to vanish from (10.), there will be no corresponding asymptotic cylinder, unless  $\varphi_{p-2}=0$ ; and in this case we must equate the coefficient of  $r^{p-3}$  in (5.) to zero, and we shall have an asymptotic cone of the third degree; and so on.

Hence, to determine the equations of the asymptotic cylinders to the surface (1.), we must find such values (if any) of  $l, m, n$  as satisfy (9.), and substitute them in (10.); if all the terms of (10.) also vanish, we must recur to the coefficient of  $r^{p-3}$  in (5.); and so on. There will be as many asymptotic cylinders as there are sets of values of  $l, m, n$  satisfying (9.), unless, after substituting any set in (10.), &c., the only term that does not vanish is that independent of  $\alpha, \beta, \gamma$ , in which case there will be no asymptotic cylinder for this set of values.

If  $\varphi_p$  contain a factor of the form  $\{\theta_q\}^2$ , the first four equations of (9.) will be satisfied by  $\theta_q=0$ ; and this, combined with  $\varphi_{p-1}=0$ , will give determinate values for the ratios  $l:m:n$ , and the corresponding asymptotic cylinders will be determined in the way just mentioned. It may happen however that  $\theta_q$  is also a factor of  $\varphi_{p-1}$ ; and if so, all the equations (9.) will be satisfied by  $\theta_q=0$ , and (10.) now admits of simplification as follows. Let

$$\varphi_p = \{\theta_q\}^2 \cdot \psi_{p-2q}, \text{ and } \varphi_{p-1} = \theta_q \cdot \psi'_{p-q-1},$$

then it may easily be shown that when  $\theta_q=0$ ,

$$D^2 \varphi_p = 2\psi_{p-2q} \cdot \{D\theta_q\}^2 \text{ and } D\varphi_{p-1} = \psi'_{p-q-1} \cdot D\theta_q.$$

Hence (10.) becomes

$$\psi_{p-2q} \cdot \{D\theta_q\}^2 + \psi'_{p-q-1} \cdot D\theta_q + \varphi_{p-2} = 0;$$

that is,

$$\left. \begin{aligned} & \psi_{p-2q} \cdot \left\{ \frac{d\theta_q}{dl} \alpha + \frac{d\theta_q}{dm} \beta + \frac{d\theta_q}{dn} \gamma \right\}^2 \\ & + \psi'_{p-q-1} \left\{ \frac{d\theta_q}{dl} \alpha + \frac{d\theta_q}{dm} \beta + \frac{d\theta_q}{dn} \gamma \right\} + \varphi_{p-2} = 0; \end{aligned} \right\} \quad \dots \quad (11.)$$

which evidently denotes two parallel cylindrical asymptotic planes; also since  $l, m, n$  are here only connected by the equation  $\theta_q = 0$ , it appears that there are in general two cylindrical asymptotic planes parallel to every tangent plane of the cone  $\theta_q(xyz) = 0$ .

Generally, let  $\{\theta_q\}^s, \{\theta_q\}^{s-1}, \{\theta_q\}^{s-2}, \dots, \theta_q$  be factors of  $\varphi_p, \varphi_{p-1}, \varphi_{p-2}, \dots, \varphi_{p-s+1}$ , and put

$$\varphi_p = \psi \cdot \{\theta_q\}^s, \varphi_{p-1} = \psi' \cdot \{\theta_q\}^{s-1}, \varphi_{p-2} = \psi'' \cdot \{\theta_q\}_{s-2} \dots \varphi_{p-s+1} = \psi^{(s-1)} \cdot \theta_q$$

(here the subscribed letters relative to  $\psi, \psi', \&c.$  are omitted for simplicity), then it may easily be shown that when  $\theta_q = 0$ , we have

$$D\varphi_p = 0, D^2\varphi_p = 0, \dots, D^{s-1}\varphi_p = 0, D^s\varphi_p = 2.3\dots s \cdot \psi \cdot \{D\theta_q\}^s, \&c.$$

Moreover, the equation to the asymptotic cylinder parallel to a generator of the cone  $\theta_q(xyz) = 0$ , will, by equating to zero the first coefficient of (5.) that does not vanish independently of  $\alpha, \beta, \gamma$ , be found to be

$$\frac{1}{2.3\dots s} D^s \varphi_p + \frac{1}{2.3\dots (s-1)} D^{s-1} \varphi_{p-1} + \dots + D\varphi_{p-s+1} + \varphi_{p-s} = 0;$$

and this, by what precedes, reduces to

$$\left. \begin{aligned} & \psi \cdot \{D\theta_q\}^s + \psi' \cdot \{D\theta_q\}^{s-1} + \psi'' \cdot \{D\theta_q\}^{s-2} + \dots \\ & + \psi^{(s-1)} \cdot D\theta_q + \varphi_{p-s} = 0. \end{aligned} \right\} \quad \dots \quad (12.)$$

Since

$$D\theta_q = \frac{d\theta_q}{dl} \alpha + \frac{d\theta_q}{dm} \beta + \frac{d\theta_q}{dn} \gamma,$$

it is evident that the asymptotic cylinder degenerates into  $s$  cylindrical asymptotic planes, all parallel to a tangent plane of the cone  $\theta_q(xyz) = 0$ ; and there is in general the same number parallel to every tangent plane of this cone.

The asymptotes to the surface (1.) passing through a given point  $(\alpha \beta \gamma)$  will be found by determining the ratios  $l:m:n$  by (4.) and (6.), and substituting, in succession, each set of

simultaneous values in (2.); the resulting equations will be those of the asymptotes to the surface that pass through the point  $(\alpha\beta\gamma)$ .

Since (4.) is of the  $p$ th degree and (6.) of the  $(p-1)$ th, the equation resulting from the elimination of  $l$  (suppose) from (4.) and (6.) cannot exceed the  $p(p-1)$ th degree, and consequently there cannot be more than  $p(p-1)$  values of the ratio  $m+n$ . From this we learn, that through any point in space there cannot be drawn more than  $p(p-1)$  asymptotes to a surface of the  $p$ th degree.

This theorem suffers an exception, however, which I proceed to consider.

It may happen that the point  $(\alpha\beta\gamma)$  through which the asymptotes are to be drawn may be so taken as to cause (4.) and (6.) to have a common factor  $\chi_q$  (which I shall suppose to be their greatest common measure). In this case (4.) and (6.) will be satisfied if  $\chi_q=0$ ; and eliminating  $l, m, n$  from this equation by means of (2.), we have

$$\chi_q(x-\alpha, y-\beta, z-\gamma)=0$$

for the equation to the asymptotic cone, which is the locus of the innumerable asymptotes that pass through the point  $(\alpha\beta\gamma)$ . (The factor  $\chi_q$  may sometimes be resolvable into other factors, and then the preceding asymptotic cone of the  $q$ th degree will in fact consist of several cones of inferior degrees.)

The division of (4.) and (6.) by  $\chi_q$  will give two equations,  $\chi'_{p-q}=0$ , and  $\chi''_{p-q-1}=0$ , which admit of no common measure. Now (4.) and (6.) will be satisfied by these two equations; but the equations  $\chi'_{p-q}=0$ ,  $\chi''_{p-q-1}=0$ , will determine not more than  $(p-q)(p-q-1)$  sets of values of the ratios  $l+m+n$ , hence (excluding the generators of the cone corresponding to  $\chi_q$ ) not more than  $(p-q)(p-q-1)$  asymptotes can pass through the point  $(\alpha, \beta, \gamma)$ .

In order to find those points (if any) which are the vertices of asymptotic cones, eliminate one of the quantities  $l, m, n$  from (4.) and (6.), and find those values of  $\alpha, \beta, \gamma$  that will render all the coefficients of the resulting equation equal to zero. If no such values be possible, the surface (1.) does not admit of an asymptotic cone; but if values  $\alpha_1, \beta_1, \gamma_1$  of  $\alpha, \beta, \gamma$  can be found, then the point  $(\alpha_1 \beta_1 \gamma_1)$  will be the vertex of an asymptotic cone. To find the equation of this cone, we must substitute  $\alpha_1, \beta_1, \gamma_1$  for  $\alpha, \beta, \gamma$  in (6.), and ascertain  $\theta_q$  the common measure of (4.) and (6.) thus modified; then will  $\theta_q(x-\alpha_1, y-\beta_1, z-\gamma_1)=0$  be the equation to the asymptotic cone, having its vertex at the point  $(\alpha_1 \beta_1 \gamma_1)$ . If the equation resulting from the elimination of  $l, m$ , or  $n$  from (4.) and (6.) can be rendered identically

zero by other simultaneous values of  $\alpha, \beta, \gamma$ , there will be as many asymptotic cones as there are sets of values. When the elimination referred to above is effected by the process for the common measure, the factor  $\theta_q$  will be the last of the remainders that do not vanish when  $\alpha_1, \beta_1, \gamma_1$  are substituted for  $\alpha, \beta, \gamma$ . It will sometimes be found, however, that (4.) and (6.) have a common measure independently of  $\alpha, \beta, \gamma$ , arising from  $\{\theta_q\}^2$  and  $\theta_q$  being factors of  $\phi_p$  and  $\phi_{p-1}$ ; and in this case we must proceed with this common measure in the way to be noticed presently.

When we know that (4.) cannot be resolved into factors, the determination of the asymptotic cone is very easy; for since (4.) admits of no measure but itself, and (6.) is of an *inferior degree*, it is evident that if there be an asymptotic cone, (6.) must be identically zero; hence if such values  $\alpha_1, \beta_1, \gamma_1$  can be given to  $\alpha, \beta, \gamma$  as to cause the coefficients of (6.) to vanish, there will be an asymptotic cone of the  $p$ th degree, namely,

$$\phi_p(x - \alpha_1, y - \beta_1, z - \gamma_1) = 0;$$

but if the coefficients cannot be rendered zero simultaneously, there will be no asymptotic cone. Since  $\alpha, \beta, \gamma$  enter (6.) in the first degree only, there will evidently be at most only one set of values of  $\alpha, \beta, \gamma$  that will render (6.) identically zero; and hence a surface of the  $p$ th degree *may* have one asymptotic cone of the  $p$ th degree, but not more, and it is plain that there cannot be an asymptotic cone of a higher degree.

If (4.) admits of being resolved into factors, and these factors can be found, the asymptotic cones may be determined as follows. Let  $\theta_q$  be one of the factors of  $\phi_p$ , and let  $\theta_q$  itself be irresolvable into factors. Arrange (6.), or rather (8.), and  $\theta_q$  according to the powers of either  $l, m$  or  $n$  ( $l$  suppose), and divide the former by the latter until the remainder is of lower dimensions in  $l$  than  $\theta_q$ ; then since  $\theta_q$  is irresolvable into factors, it is clear that this remainder must be identically zero: find therefore  $\alpha_1, \beta_1, \gamma_1$ , the values of  $\alpha, \beta, \gamma$ , that make the coefficients of the remainder vanish, then  $\theta_q(x - \alpha_1, y - \beta_1, z - \gamma_1) = 0$  will be the asymptotic cone. As  $\alpha, \beta, \gamma$  enter (8.) in the first degree and do not enter  $\theta_q$ , there cannot be more than one set of values of  $\alpha, \beta, \gamma$ , if indeed there be any. The same process being repeated with each of the other prime factors into which (4.) is resolvable, we shall have all the asymptotic cones which the surface admits of.

The preceding process requires modification when the second or any higher power of  $\theta_q$  is a factor of  $\phi_p$ . As an example, suppose that  $\{\theta_q\}^4$  enters as a factor into  $\phi_p$ , and put  $\phi_p = \psi \cdot \{\theta_q\}^4$  ( $\theta_q$  not being a factor of  $\psi$ ). When  $\theta_q = 0$ ,  $D\phi_p$

$+\varphi_{p-1}=0$ , reduces to  $\varphi_{p-1}=0$ , and consequently there will be no asymptotic cone unless  $\theta_q$  be a factor of  $\varphi_{p-1}$ ; if so, let  $\varphi_{p-1}=\psi \cdot \theta_q$ , then

$$\frac{1}{2} D^2 \varphi_p + D \varphi_{p-1} + \varphi_{p-2} = 0$$

becomes  $\psi \cdot D\theta_q + \varphi_{p-2} = 0$ , which is of the first degree in  $\alpha, \beta, \gamma$ , and this (instead of (8.)) being combined with  $\theta_q=0$ , may give an asymptotic cone. If  $\{\theta_q\}^2$  however be a factor of  $\varphi_{p-1}$ , then

$$\frac{1}{2} D^2 \varphi_p + D \varphi_{p-1} + \varphi_{p-2} = 0$$

becomes  $\varphi_{p-2}=0$ , and there will be no asymptotic cone unless  $\theta_q$  be a factor of  $\varphi_{p-2}$ . If this be the case, assume  $\varphi_{p-1}=\psi \cdot \{\theta_q\}^2$ , and  $\varphi_{p-2}=\psi'' \cdot \theta_q$ , then

$$\frac{1}{2.3} D^3 \varphi_p + \frac{1}{2} D^2 \varphi_{p-1} + D \varphi_{p-2} + \varphi_{p-3} = 0$$

reduces to

$$\psi \cdot \{D\theta_q\}^2 + \psi'' \cdot D\theta_q + \varphi_{p-3} = 0;$$

and this equation, which replaces (8.), combined with  $\theta_q=0$ , may give one or two asymptotic cones (but not more, as will be shown below), unless  $\theta_q$  should enter both  $\varphi_{p-1}$  and  $\varphi_{p-2}$  in a higher power than has been supposed; we shall then have  $\varphi_{p-3}=0$ ; and hence  $\theta_q$  must (if there be an asymptotic cone) be a factor of  $\varphi_{p-3}$ . Suppose therefore

$$\varphi_{p-1}=\psi \cdot \{\theta_q\}^3, \quad \varphi_{p-2}=\psi'' \cdot \{\theta_q\}^2, \quad \text{and} \quad \varphi_{p-3}=\psi''' \cdot \theta_q,$$

then

$$\frac{1}{2.3.4} D^4 \varphi_p + \dots + \varphi_{p-4} = 0$$

becomes

$$\psi \cdot \{D\theta_q\}^4 + \psi \cdot \{D\theta_q\}^3 + \psi'' \cdot \{D\theta_q\}^2 + \psi''' \cdot D\theta_q + \varphi_{p-4} = 0;$$

and this equation (which cannot be satisfied independently of  $\alpha, \beta, \gamma$ , for  $\theta_q$  is not a factor of  $\psi$ ), combined with  $\theta_q=0$ , may give four asymptotic cones.

Similarly, if  $\{\theta_q\}^s$  be the highest power of  $\theta_q$  that is a factor of  $\varphi_p$ , it may be shown that  $\alpha, \beta, \gamma$  enter the equation to be combined with  $\theta_q=0$ , only through  $D\theta_q$ , and that this equation may rise to any degree in  $D\theta_q$  (except the  $(s-1)$ th) not exceeding  $s$ .

Hence when a power  $(s)$  of  $\theta_q$  is a factor of  $\varphi_p$ , we must ascertain the highest powers of  $\theta_q$  that are factors of  $\varphi_{p-1}, \varphi_{p-2}, \dots, \varphi_{p-t+1}$ , also  $\varphi_{p-t}$  the first term of (1.) that has not  $\theta_q$  for a factor; we must then equate to zero the coefficient (reduced as above) of the highest power of  $r$  in (5.) that does not vanish independently of  $\alpha, \beta, \gamma$ . If  $\alpha, \beta, \gamma$  disappear from this equation

so that it becomes  $\phi_{p-t}=0$ , there will be no asymptotic cone; but if this be not the case, then the reduced equation must be combined with  $\theta_q=0$ , in the same way as directed for (8.) and  $\theta_q=0$ , and we may get asymptotic cones though not more than  $s$  of them. I proceed to establish the last assertion.

It has been shown above that if  $\{\theta_q\}^s$  be the highest power of  $\theta_q$  that is a factor of  $\phi_p$ , then the equation to be combined with  $\theta_q=0$  will be of the form

$$\psi \cdot \{D\theta_q\}^t + \psi' \cdot \{D\theta_q\}^{t-1} + \dots = 0, \dots \quad (13.)$$

where  $\psi, \psi \dots$  do not involve  $\alpha, \beta, \gamma$ , and  $t$  may be equal to, but cannot be greater than  $s$ . Now if there be a corresponding asymptotic cone, let  $(\alpha_1, \beta_1, \gamma_1)$  denote its vertex; then if

$$\frac{d\theta_q}{dl} \alpha_1 + \frac{d\theta_q}{dm} \beta_1 + \frac{d\theta_q^s}{dn} \gamma_1$$

(which I shall denote by  $D_1\theta_q$ ) be substituted for  $D\theta_q$  in (13.), the resulting equation will be satisfied by aid (if necessary) of  $\theta_q=0$ ; hence (13.) must be divisible by  $D\theta_q - D_1\theta_q$ , so that it may be written

$$(D\theta_q - D_1\theta_q)(\psi \cdot \{D\theta_q\}^{t-1} + \dots) = 0. \dots \quad (14.)$$

Also, if  $\alpha_2, \beta_2, \gamma_2$  be another set of values of  $\alpha, \beta, \gamma$ , satisfying (13.), they must reduce the second factor of (14.) to zero, for the first is of a lower degree than  $\theta_q$ . Hence  $\psi \cdot \{D\theta_q\}^{t-1} + \dots$  must be divisible by  $D\theta_q - D_2\theta_q$ , and so on. In this way we shall, after a certain number ( $v$ ) of divisions, get an equation,

$$\psi \cdot \{D\theta_q\}^{t-v} + \dots = 0,$$

which either does not contain  $D\theta_q$  (and hence  $\alpha, \beta, \gamma$ ) at all, or which cannot be satisfied by any values of  $\alpha, \beta, \gamma$ . Rejecting this factor then as affording no solution, (13.) is equivalent to

$$(D\theta_q - D_1\theta_q)(D\theta_q - D_2\theta_q) \dots (D\theta_q - D_v\theta_q) = 0,$$

and each of these factors will give but one set of values of  $\alpha, \beta, \gamma$ ; hence there will be but  $v$  asymptotic cones,

$$\theta_q(x-\alpha_1, y-\beta_1, z-\gamma_1) = 0 \dots \theta_q(x-\alpha_v, y-\beta_v, z-\gamma_v) = 0;$$

and since  $v$  cannot exceed  $t$ , nor  $t$  exceed  $s$ , it follows that there cannot be more than  $s$  asymptotic cones resulting from a factor of  $\phi_p$  of the form  $\{\theta_q\}^s$ .

When  $\theta_q$  is of the first degree, it is clear that instead of an asymptotic cone we shall have a plane; and since any point in it may be regarded as the vertex, every straight line drawn in it will be an asymptote; hence the asymptotic cone will in this case become a conical asymptotic plane: also since  $\theta_q$  is here of the form  $A\alpha + B\beta + C\gamma$ ,

$$D\theta_q = A\alpha + B\beta + C\gamma,$$

which does not involve  $l$ ,  $m$  or  $n$ . Hence to determine the conical asymptotic planes (if any) to the surface (1.), we must take those factors of  $\varphi_p$  that are of the first degree, and proceed as directed above for asymptotic cones; with this modification, however, that  $D\theta_q$  not containing  $l$ ,  $m$  or  $n$  must be regarded as a single constant, and consequently the process will be much simplified. If  $V_1, V_2 \dots V_t$  ( $t$  not  $\rightarrow s$ ) be the values of  $D\theta_q$  corresponding to the factor

$$\{\theta_q\}^s = \{Al + Bm + Cn\}^s,$$

we shall have

$Ax + By + Cz = V_1, Ax + By + Cz = V_2 \dots Ax + By + Cz = V_t$ . as the equations to the conical asymptotic planes relative to this factor.

It appears from the preceding reasoning, that if the equation (4.), or, which is the same thing, the highest homogeneous function in the equation to the surface (1.) can be resolved into  $a$  factors of the first degree,  $b$  factors of the second degree,  $c$  factors of the third degree, &c. (here a factor of the form  $\{\theta_q\}^s$  is to be accounted  $s$  factors), then the surface may admit of, but cannot have more than  $a$  asymptotic cones of the first degree, that is,  $a$  conical asymptotic planes,  $b$  asymptotic cones of the second degree,  $c$  asymptotic cones of the third degree, &c. Some of these cones may have the same vertex; and since  $a + 2b + 3c \dots = p$ , the degree of the aggregate of all the asymptotic cones to a surface can never exceed that of the surface itself.

It will be seen that unless equal factors enter the highest homogeneous function, the asymptotic cones to a surface depend only on the two highest homogeneous functions in its equation; and hence (the above case excepted) all surfaces having the two highest homogeneous functions in their equations identical, will have the same asymptotic cones. Also conversely, it is plain that those surfaces that have the same asymptotic cones must have the two highest homogeneous functions in their equations identical, providing the degree of the equations to the surfaces be exactly equal to that of the aggregate of the cones. Now this aggregate may be considered one of these surfaces; hence if

$$u_1 = 0, u_2 = 0, \dots, u_t = 0$$

be the equations to cones, the aggregate of which is of the  $p$ th degree, the equation to all the surfaces of the  $p$ th degree having these for asymptotic cones may be denoted by

$$u_1 u_2 \dots u_t + \chi_{p-2}(xyz) + \chi_{p-3}(xyz) \dots + \chi_1(xyz) + \chi_0 = 0. \quad (15.)$$

Wimbledon, Surrey, Nov. 10, 1847.

**LXVII. On the Chemical Composition of the Substances employed in Pottery. By Mr. R. A. COUPER\*.**

**A**LL kinds of earthenware are composed of two parts, viz. the body and the glaze.

The body is the principal part of the vessel, being the base or foundation, as indicated by the term itself. The glaze is a thin transparent layer of glass which covers the body and fills up its pores, giving it a smooth surface with a polished and a finished appearance.

I. The substances principally employed to form the body of earthenware are, clays of different kinds, flint and Cornish stone.

Clay which constitutes the base of the body of earthenware is distinguished from siliceous earth by becoming plastic when mixed with water, and being very soft and not gritty to the feel; also when burned, it keeps its form, and becomes firm and solid; whereas siliceous earth crumbles into a powder when burned. Clay when intensely heated, as in porcelain manufactories, does not regain its plasticity, which it loses in the burning, although pounded very fine, in which state it is technically termed potsherd.

Clay is obtained naturally from Cornwall, Dorset, and Devonshire, and is the finer particles of decomposed felspar deprived of its alkali.

1. The finest clay (termed *China clay*) used in Britain is obtained artificially from Cornwall, by running a stream of water over decomposed granite, which carries with it the finer particles of felspar, and is then received into catchpools or ponds where it is allowed to subside. The water is then run off, leaving a fine sediment, which is removed and exposed to the atmosphere for four or five months, when it is ready for export. By analysis of this clay previously dried at  $212^{\circ}$ , I found it to consist of—

	I.	II.
Silica . . . . .	46·32	46·29
Alumina . . . . .	39·74	40·09
Protoxide of iron . . . . .	·27	·27
Lime . . . . .	·36	·50
Magnesia . . . . .	·44	
Water and some alkali	<u>12·67</u>	<u>12·67</u>
	99·80	99·82

For the second analysis I am indebted to Mr. John Brown. The more common clays, which are found naturally depo-

\* Read before the Philosophical Society of Glasgow, April 28, 1847, and communicated by Dr. R. D. Thomson.

sited, are supposed to have been produced in a similar manner to the china clay ; the rains having washed from the hills the decomposed rock into a lake or estuary, where it has subsided and gradually displaced the water, and become in the course of time perfectly firm and solid, forming fields of clay. The clay is found in layers or strata lying over each other, each layer possessing some distinctive property from the other, which renders each clay fitted for a peculiar purpose.

2. *Sandy clay* (stiff or ball) is the upper layer of clay, and is used by itself for making salt glazed ware ; it is well adapted for this kind of ware, in consequence of the considerable quantity of silica or sand which it contains. By analysis of this clay, I found it to be composed of—

Silica . . . . .	66·68
Alumina . . . . .	26·08
Protioxide of iron . . . . .	1·26
Lime . . . . .	·84
Magnesia . . . . .	trace
Water . . . . .	5·14
	<hr/>
	100·00

being previously dried at 212°, specific gravity = 2·558.

3. *Pipe clay* is the second layer, which is used in making tobacco pipes. This clay is not employed in manufacturing earthenware, owing to its possessing the property of contracting more than sandy clay. It was analysed by Mr. John Brown, who obtained—

Silica . . . . .	58·66
Alumina . . . . .	32·00
Protioxide of iron . . . . .	1·35
Lime . . . . .	·40
Magnesia . . . . .	trace
Water . . . . .	12·08
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	99·49

4. *Blue clay* is of a grayish colour, and is considered the best layer of clay in the whole series, owing to its burning perfectly white, and approaching in character nearest to the china clay. As analysed by Mr. John Higginbotham, it was found to consist of—

Silica . . . . .	46·38
Alumina . . . . .	38·04
Protioxide of iron . . . . .	1·04
Lime . . . . .	1·20
Magnesia . . . . .	trace
Water . . . . .	13·57
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	100·23

also previously dried at 212°. There is a variety of other clays obtained from these fields, which are of less value, and need not be enumerated here, as they are similar in appearance to those already noticed.

5. *Red or brown clay*, which is very abundant in the neighbourhood of Glasgow, is a surface clay, and contains a large quantity of peroxide of iron, which gives it a deep brown colour. It is of this clay that common black ware, flower-pots, and red bricks are made, which do not require a very high temperature, else they would fuse. The analysis gave—

Silica . . . . .	49·44
Alumina . . . . .	34·26
Protoxide of iron . . . . .	7·74
Lime . . . . .	1·48
Magnesia . . . . .	1·94
Water . . . . .	5·14
<hr/>	
	100·00

6. *Yellow clay* is obtained from various parts of the country, and is so called from possessing a yellow colour both before and after being burned, owing to the presence of iron.

By mixing sandy clay and red clay together, we gain an artificial yellow clay, which is often employed.

Yellow clay, as analysed by Mr. John Brown, was found to contain—

Silica . . . . .	58·07
Alumina . . . . .	27·38
Protoxide of iron . . . . .	3·30
Lime . . . . .	·50
Water . . . . .	10·30
Magnesia . . . . .	trace
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	99·55

7. *Fire-clay* is also very abundant in this country, and occurs both on the surface and several fathoms under ground. It is termed marl, and is used principally in potteries for making saggars or vessels for placing the ware previous to burning to protect them from the flame; and owing to its coarse particles, which cause the body to be very porous, is well adapted for strong heats: crucibles, or large pots for glass works, in which the glass is fused, are also made from fire-clay, as well as bricks known under the name of fire-brick. This clay was analysed by Mr. John Brown, who obtained—

Silica . . . . .	66·16
Alumina . . . . .	22·54
Protoxide of iron . . . . .	5·31
Lime . . . . .	1·42
Magnesia . . . . .	trace
Water . . . . .	3·14
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	98·57

8. *Flint* as used in potteries is first calcined, then water-ground, in which state it is used for mixing with clays, and is called slop flint; but for glazes it is evaporated to dryness, and used in the dry state with other articles which constitute the glaze.

9. Cornish stone or granite is water-ground, then evaporated to dryness for mixing in glazes, and is used in the slop state for mixing with clays.

10. Plaster of Paris or gypsum, which is employed in forming the moulds in which certain kinds of pottery are cast, is a native sulphate of lime. It is a very important article to the manufacturer of earthenware, owing to its singular property of parting easily with the clay by the application of a slight heat. Plaster of Paris requires to be dried at a high temperature before using it; but if it is over-dried, it will not again set for making moulds; the drier the stucco the harder are the moulds that are made of it, and they will stand more readily a greater degree of wear. Plaster of Paris casts, as commonly prepared, cannot again be used for the same purpose.

II. The colours used for printing and painting on ware are similar to one another, excepting that the colours for painting may not be so expensive as for printing; both however form an important and extensive part of the materials of a pottery. The manufacturers of earthenware are much occupied with the improvement of the variety and beauty of the colours, as well as of the patterns or styles that are produced, and hence a great emulation exists among those employed in the trade.

1. The blue colour in printing is produced from cobalt, which is used with flint, ground glass, pearlash, white lead, barytes, china clay, and oxide of tin in reducing its strength.

2. The brown colour by ochre, manganese, and cobalt.

3. The black colour by chromate of iron, nickel, ironstone, and cobalt.

4. The green colour by chrome, oxide of copper, lead, flint, and ground glass.

5. The pink colour by chrome, oxide of tin, whiting, flint ground glass, and china clay, which are mixed in various proportions, fused together at a high temperature, then pounded and mixed with oil, when it is ready for the printer's use.

For the following analysis of a blue cobalt calx, I am indebted to Mr. John Adam:—

Silica . . . . .	17·84
Peroxide of cobalt . . . . .	19·42
Peroxide of iron . . . . .	25·50
Water . . . . .	8·41
Carbonate of lime and magnesia .	<u>28·45</u>
	99·62

The oil that is used for mixing with the colours, is made by boiling the following substances together; viz. linseed oil, rape oil, sweet oil, rosin, common tar, and balsam copaiba in various proportions.

III. It is but recently since a new method has been applied to cause the colours to flow or spread over the surface of the ware. This object is effected by washing the saggars in which the ware is placed previous to its being fired in the glost kiln, with a mixture of—

1. Lime, common salt, and clay slip. Dry flows are also used, which answer equally well, the mixture being sprinkled on the bottom of the saggars. The following are some of those flows:—

2. Lime, sal-ammoniac and red lead.

3. Lime, common salt, and soda.

4. Whiting, lead, salt and nitre.

5. But there is a wash made of lime, clay slip, nitre, salt, lead, in general use for washing all the saggars employed in the glost kiln, which fuses on the inner surface of the saggars, making it perfectly close and not porous, otherwise the gloss required on the surface of the ware would not be obtained.

IV. The colours used in producing the dipt or sponged ware are of a very cheap kind, as it is only for common purposes that they are employed. The colours when used for dipt ware are put on the ware before it is burned; and when used for sponged ware, are put on the ware in the biscuit state. The following are some of those colours:—

1. A black dip is made from manganese, ironstone and clay slip.

2. A drab dip by nickel and slip.

3. A sage or a greenish-blue dip by green chrome and slip.

4. A blue dip by cobalt and clay slip.

5. A yellow dip by yellow clay alone, or a compound of white and red clay, which produces the same results.

6. A red dip is produced from the red or brown clay; but it is not every quality of this clay that will answer, as it requires to burn red.

The first four of these dips are prepared by mixing a little

of the colouring agent with a quantity of clay slip ; whilst the two last-mentioned dips are mixed with water to produce the slip state, in which state they are employed.

V. There are several kinds of bodies manufactured ; but they may be all classed under two heads, viz. porcelain and earthenware.

1. *Porcelain or china* is a rich, very smooth and transparent ware, and is the finest quality that has yet been manufactured. It is a fused body, and owes its transparency to this circumstance ; it also requires a very high temperature to burn it, and is manufactured in this country from flint, Cornish stone (granite), china clay, and bone-earth ; the lime employed acting as a flux, partly fusing it. By analysis of two pieces of china from different manufactories in Staffordshire, I found them to be differently composed. The last of these pieces was also analysed by Mr. Crichton, the three analyses being as follows :—

	No. 1, by R. A. C.	No. 2, by R. A. C.	No. 2, by W.C.
Silica . . . . .	39·88	40·60	39·685
Alumina . . . . .	21·48	24·15	24·650
Lime . . . . .	10·06	14·22	14·176
Protoxide of iron } Phosphate of lime }	26·44	15·32	15·386
Magnesia . . . . .	.....	·43	·311
Alkali or difference	2·14	5·28	5·792
	100·00	100·00	100·000

2. Foreign manufacturers do not employ bone-earth ; but instead of it they use felspar, the alkali of which supplies the place of the phosphate of lime. The Germans make the best porcelain for chemical purposes, as that body is more vitrified and less liable to be acted upon by acids, as well as being capable of standing a very strong heat ; and hence it is extensively used by chemists. By the analysis of some specimens of foreign porcelain, I obtained the following results :—

	Berlin.	Chinese Porcelain, superior.	inferior.
Silica . . . . .	72·96	71·04	68·96
Alumina and protoxide of iron	24·78	22·46	29·24
Lime . . . . .	1·04	3·82	1·60
Alkali . . . . .	1·22	2·68	
	100·00	100·00	99·80
Specific gravity . . . . .	2·419	2·314	2·314

VI. Earthenware is a very porous and less compact body than china or porcelain, owing to its containing little or no alkali, which is the great difference between these bodies. I had a piece of ware manufactured, resembling in appearance porcelain, as regards the absence of porosity and its compactness,

slightly transparent, and capable of standing a very strong and sudden heat; it was produced by mixing soda to the extent of  $3\frac{1}{2}$  per cent. in a little clay prepared for the common white body, and was then fired in the biscuit kiln. The clay employed having been previously well dried, so as to weigh it without water, the proportional quantity of soda requisite was then calculated and weighed out; the clay was again mixed with water along with the soda; it was then formed into capsules, which after being fired and then broken, presented the appearance of a vitrified or fused body.

1. The common white ware or earthenware is made from flint, Cornish stone, china clay, and blue clay, and does not require such a high temperature in burning as the porcelain does. By analysis of a piece of white ware manufactured in this city, it was found to contain—

Silica . . . . .	68·55
Alumina and protoxide of iron .	29·13
Lime . . . . .	1·24
	98·92
Specific gravity . . . . .	2·36

Coloured ware is also manufactured from the same substances, but mixed with a colouring agent which stains the body.

2. The toqua or blue-coloured ware is coloured by cobalt.  
3. The sage or greenish-blue coloured ware, by nickel and cobalt.

4. The drab or buff-coloured ware by chromate of iron.  
5. The body for the cane or yellow-coloured ware is produced by a mixture of sandy clay and common red clay, the same as used for red bricks, but is generally produced from the natural yellow clay found in particular localities.

6. The last-mentioned body is also employed for making Rockingham ware, which only varies from the cane ware by possessing a different glaze.

7. The common black ware body is made from the red clay alone.

8. The Egyptian ware body is made from ironstone, ball and red clay.

These four last-mentioned bodies are not nearly so expensive as the white ware, and do not require nearly such a high temperature to burn them; therefore they are, comparatively speaking, soft bodies.

9. Salt glazed ware is made from sandy clay and a little sand, to keep the body open, or make it less compact; but for large salt glazed ware, potsherd, which is ware that has

been fired and then ground, is employed to render the body still more open or porous, and also to give it a greater capability of standing sudden heats or colds. This ware is much used in public works for chemical purposes: it is exposed to the action of the flame during burning, whereas other kinds of ware are protected by saggars from the flames.

VII. The glaze vitrifies the surface of the body, rendering it generally capable of withstanding acids. It is a very important point with the manufacturer to obtain a glaze which will adhere to the body without crazing or peeling off, as he may discover a good body, but not find a glaze to answer it, since every glaze will not adhere to the same body, and hence every manufacturer has a glaze of his own composition.

1. The substances used in the preparation of the glaze for white ware, are borax, china clay, flint, Cornish stone, Paris white, and white lead.

In preparing the glaze, a substance technically termed frett is first made, consisting of borax, china clay, flint, Cornish stone, and Paris white, which are fused together in a kiln, and when ready allowed to flow into water, which shortens it, owing to the water being mechanically lodged in it, and keeps it from adhering to the bottom of the vessel, rendering it much easier to pound. Frett is a beautiful glass, coloured by a little iron, and is pounded and water-ground along with Cornish stone, flint, and white lead: this constitutes the glaze for white ware.

	Analysis of white glaze.	Analysis of frett.
Silica . . . . .	43.66	55.98
Lime . . . . .	.52	2.52
Alumina and protoxide of iron	9.56	10.38
Borax . . . . .	20.08	31.12
Carbonate of lime . . . . .	10.88	
Carbonate of lead . . . . .	15.19	
	<hr/> 99.89	<hr/> 100.00
Specific gravity . . . . .		2.345

A piece of earthenware was brought from America, having been discovered several feet under ground, the glaze of which was tested, and found to be composed of silica, iron, alumina, lime, sulphate of lime and antimony, which was a beautiful rich white glaze concealing a common red clay body.

2. The glaze of Rockingham ware possesses a beautiful brownish metallic lustre, and is made from Cornish stone, flint, manganese, red lead and clay slip, the latter substance being a little clay mixed with water until it becomes of the consistency of milk.

3. The glaze for common black ware is made from the same

materials in different proportions, and has a brilliant black appearance.

4. The glaze used for cane or yellow-coloured ware is made from flint, red lead, and Cornish stone.

5. The Egyptian ware owes its value to the beautiful and rich tinted black glaze, made from flint, Cornish stone, red lead, and manganese, with which it is covered.

These four last-mentioned glazes are made by stirring the substances together with a certain quantity of water, and passing it through a very fine sieve or search. Glazes do not require such a high temperature to fuse them on the surface of the ware, as the body does to be burned.

6. The glaze for salt glazed ware is common salt, which is thrown in at the top of the kiln through a number of small apertures in the crown of it, and diffuses itself through all parts of the kiln, giving the ware the required glaze. The action that is supposed to take place, when the salt is thrown into the kiln, is owing to its decomposition. The chlorine of the salt combines with the hydrogen of the water, which is mechanically lodged in the salt, forms muriatic acid gas, which passes off, while the sodium combining with the oxygen of the water then unites with the silica in the ware, forming a silicate of soda which fuses on its surface. The salt is not thrown in until the kiln has been raised to its greatest necessary temperature.

Table of the Composition of Clays and Porcelain when free from Water.

	Silica.	Alumina.	Protoxide of iron.	Lime.	Magnesia.	Phosphate of lime and protoxide of iron.	Alkali and loss.	Specific gravity.
Cornish china clay .....	53.16	45.61	.31	.41	.51			
Cornish china clay .....	53.12	46.00	.31	.57	.51			
Sandy clay .....	70.29	27.47	1.33	.90	Trace	.....	.....	2.558
Pipe clay .....	61.39	36.61	1.54	.46	Trace			
Blue clay .....	53.52	43.89	1.20	1.39	Trace			
Red clay .....	52.11	36.19	8.17	1.56	2.04			
Fire clay .....	69.33	23.62	5.56	1.49	Trace			
Yellow clay .....	65.06	30.68	3.70	.56	Trace			
English china ware, No. 1 ...	39.88	21.48	.....	10.06	Trace	26.44	2.14	
... No. 2 ...	40.60	24.15	.....	14.22	.43	15.32	5.28	
... No. 2 ...	39.68	24.65	.....	14.18	.31	15.39	5.79	
Berlin ware .....	72.96	24.78	...	1.04	Trace	.....	1.22	2.419
Superior Chinese ware .....	71.04	22.46	...	3.82	Trace	.....	2.68	2.314
Inferior Chinese ware .....	68.96	29.24	...	1.60	Trace	.....	.....	2.314
Common English white ware	68.55	29.13	...	1.24	Trace	.....	.....	2.360

LXVIII. *On the Polarization of the Atmosphere.* By Sir DAVID BREWSTER, K.H., D.C.L., F.R.S., and V.P.R.S. Edin.\*

**W**HEN the light of the sun or of any self-luminous body has been transmitted through certain crystallized substances, or has been reflected from, or refracted by, bodies not metallic, it suffers a physical change, to which the name of *plane polarization* has been given. This physical change consists in decomposing common light into two equal portions of polarized light, one of which is polarized in a plane at right angles to that in which the other is polarized. In doubly refracting crystals, the two pencils are polarized in opposite or rectangular planes; and when common light is reflected from any body not metallic, whether it is solid, or fluid, or gaseous, a portion of the incident light enters the body; and of the portions thus reflected and refracted, precisely the same quantity is polarized,—the light polarized by refraction being polarized in a plane at right angles to that which is polarized by reflexion.

If the earth had no atmosphere the sky would appear absolutely black; and when the sun sets we should be left in utter darkness. The existence of twilight, however, the blue colour of the sky, and the refraction of the rays which emanate from the stars and planets, place it beyond a doubt that the pure air in which we live and breathe is capable of acting upon light like all other bodies, and consequently of producing that physical change which constitutes *polarization*. The polarization of the blue sky, or of the atmosphere, was therefore observed and studied by different philosophers, both in France and England; and it was speedily ascertained, in conformity with the laws of polarization, that the polarization was a *minimum* in the vicinity of the sun, where his light is reflected at angles approaching to  $90^\circ$ , or where the incident and reflected rays form an angle approaching to  $180^\circ$ ; that it was also a *minimum* in the region opposite the sun, where his light is reflected at an angle approaching to  $0^\circ$ , or at a perpendicular incidence; and that it was a *maximum* in those intermediate parts of the sky, which are distant about  $90^\circ$  from the sun, and where his light is reflected at an angle of about  $45^\circ$ , the polarizing angle for *air*.

Such was the first view which was naturally taken of the

\* This paper is reprinted, with the permission of Dr. Berghaus and Mr. A. K. Johnston, from the Seventh Part of their valuable Physical Atlas now in the course of publication. A map representing the four neutral points, and the system of lines of equal polarization, will be found in that work.

polarization of the atmosphere, and a considerable time elapsed before its leading elements were determined, and its more important phenomena observed and measured. It is to M. Arago, to whom this branch of science owes such deep obligations, that we are indebted for the discovery of the first and leading fact on which the law of atmospheric polarization depends. In examining the region of the sky opposite to the sun, he discovered a *neutral point*, or a point in which there is *no polarization* whatever. This neutral point he found to be  $25^{\circ}$  or  $30^{\circ}$  above the point diametrically opposite to the sun, or what we may call the *antisolar point*; and we shall distinguish this pole of no-polarization by the name of *M. Arago's neutral point*, or the *antisolar neutral point*. It is best seen after sunset.

In the year 1840, M. Babinet discovered a second neutral point, situated about the same distance above the sun as the neutral point of M. Arago is situated above the antisolar point. This point is most distinctly seen immediately after sunset, but is generally much fainter than the other, owing to the discoloration of the blue sky by the yellow light of the setting sun.

Our readers are no doubt aware, that when light is reflected from the surfaces of transparent bodies, a certain portion of it, and at a particular angle the whole of it, is *polarized* in the plane of reflexion, or *positively*\*; while precisely the same quantity of the transmitted light is *polarized* in a plane at right angles to the plane of reflexion or refraction, or *negatively*. Now, in the part of the sky between the neutral point of M. Arago and that of M. Babinet, the light is polarized *positively*; while in the parts of the sky between the first of these neutral points and the antisolar point, or between the second and the sun, it is polarized *negatively*. Hence it became obvious that the two neutral points must be produced by a compensation, in which light polarized *negatively* neutralized light polarized *positively*, and that the *negative* light was either produced by *reflexion* in a plane at right angles to that passing through the sun, the neutral point, and the observer, or by *refraction* in a plane passing through these three points, or by both these causes combined. But in whatever way the *negative* polarization was produced, it was manifest that the same cause ought to produce a *neutral point beneath the sun*. After many fruitless attempts to discover this neutral point—owing chiefly to the predominance of the sun's light

\* These terms are used for the purpose of abbreviation. An account of the laws of the polarization of light by reflexion and refraction, will be found in my papers in the Phil. Trans., 1815, p. 129, and 1830, pp. 69, 133.

at the part of the sky where it should be found—I at last observed, under a very favourable state of the atmosphere, that the polarization of the sky was *negative* in the space between the risen sun and the horizon. This observation placed it beyond a doubt that there must be a neutral point below the sun, where that *negative* polarization passed into *positive* polarization; and by concealing the sun from view, and admitting no light to the eye but what came from the probable place of the neutral point, I succeeded in discovering it. After communicating this discovery to M. Babinet\*, early in 1845, he made several ineffectual attempts to confirm it; and it was not till the 23rd of July 1846, when the state of the sky was peculiarly favourable for the observation, that he succeeded in obtaining a distinct view of it †.

Before proceeding to explain the map of the lines of equal polarization in the pure blue sky, I shall give a brief account of my observations on the three neutral points to which I have referred :—

### I. On M. Arago's Neutral Point.

In the normal state of the lines of equal polarization, namely, when the sun is in the horizon, this neutral point is about  $18\frac{1}{2}^{\circ}$  above the horizon or above the antisolar point; but when the sun is about  $11^{\circ}$  or  $12^{\circ}$  above the horizon, and the antisolar point of course as much below it, the neutral point is in the horizon, and consequently only  $11^{\circ}$  or  $12^{\circ}$  above the antisolar point. As the sun descends to the horizon, and the antisolar point rises, the distance of the neutral point from the latter gradually increases; and when the sun reaches the horizon, the neutral point is  $18\frac{1}{2}^{\circ}$  above it, and therefore  $18\frac{1}{2}^{\circ}$  distant from the antisolar point. After the sun has set, the distance of the neutral point from the antisolar point increases; that is, it rises faster than the sun descends, and its maximum distance when the twilight is very faint, is about  $25^{\circ}$ .

In the latitude of St. Andrews, M. Arago's neutral point is above the horizon all the day between the middle of November and the end of January. In the other months of the year it

\* *Comptes Rendus des Séances de l'Acad. des Sciences*, tom. xxii. p. 801–803, 1845, 17th Mars.

† *Comptes Rendus, &c.*, Juillet 27, 1846, tom. xxiii. p. 195; and Aout 3, 1846, tom. xxiii. p. 233. “M. Brewster,” says M. Babinet, “a sans doute été guidé dans sa recherche par des vues théoriques; autrement il me paraît peu probable qu'il eut fait, par observation seul de la polarization atmosphérique, la découverte remarquable de ce point neutre si difficile à reconnaître, et que, depuis lui j'avais plusieurs fois tenté inutilement de retrouver.” *Ibid.* p. 235.

never rises till the sun is within  $11^{\circ}$  or  $12^{\circ}$  of the horizon, and never sets till the sun is  $11^{\circ}$  or  $12^{\circ}$  above the horizon.

## II. On a secondary Neutral Point accompanying M. Arago's Neutral Point.

I observed the first traces of this remarkable phænomenon on the 8th of June 1841, at  $5^{\text{h}} 50'$ , when the positive polarization was strongest close to the horizon, whether land or sea, and to about  $1\frac{1}{2}^{\circ}$  above it. Hence, when M. Arago's neutral point rose, it *did not appear first in the horizon*, but about  $1\frac{1}{2}^{\circ}$  above it, the compensation being effected where the positive polarization was weaker than in the horizon. When this took place, we had the singular phænomenon of *a neutral point with positive polarization on each side of it*. When this phænomenon was more fully developed, under a favourable state of the horizon, the positive polarization was overcome by the advancing negative polarization. The negative polarization was then immediately below the ascending neutral point; but at a certain distance, a few degrees below the neutral point, the negative polarization was compensated by the excess of positive polarization close to the horizon, and the beautiful phænomenon was seen of two neutral points separated by bands of negative polarization! This phænomenon was best seen on the sea horizon, which was marked by an obscure band a few degrees high, that indicated the existence of a distant haze. On the 21st of April 1842, I observed the secondary neutral point under favourable circumstances. At  $6^{\text{h}} 22'$  P.M., when the primary neutral point was  $15^{\circ}$  high, the secondary one was  $2^{\circ} 50'$  high. At  $7^{\text{h}}$  positive bands were still seen above the sea line, and were strongest upon the obscure band above the visible sea line.

## III. On M. Babinet's Neutral Point.

This neutral point is situated about  $18^{\circ} 30'$  above the sun, when he is rising or setting in a very clear sky. It is not so easily seen as that of M. Arago, and was therefore longer in being discovered. It is above the horizon during the greater part of the year in great latitudes, and being above the sun, it is of course always visible when the sun is above the horizon in a clear sky. When the sun is in the zenith, this neutral point coincides with the sun's centre. As the sun's altitude diminishes, it separates from the sun's centre, its distance gradually increasing till it becomes  $18^{\circ} 30'$ , when the sun's altitude is nothing, or at sunrise and sunset.

The neutral point of M. Babinet *must*, like that of M. Arago, be accompanied, in certain states of the horizontal

sky, with a secondary neutral point; but I have never had an opportunity of observing M. Babinet's neutral point when it either rose above or set beneath the horizon, which, though not essential, is the most favourable for observing a secondary neutral point.

#### IV. On the Neutral Point below the Sun.

This neutral point is, as we have previously noticed, much more difficult to be seen than that of M. Babinet. In November, December and January, it cannot be seen in our latitudes, unless when, early in November and late in January, a higher degree of polarization in the sky brings it above the horizon at noon.

As theory indicated the existence of this neutral point, I long sought for it in vain; but when I was assured of its existence by the discovery of negative polarization, which often extended from the sun to the horizon even when the sun's altitude was  $30^\circ$ , I took such precautions for excluding all unnecessary light from the eye that I at last observed it near the horizon, with a small portion of positively polarized light beneath it. I afterwards observed it repeatedly when the sun had higher altitudes, and was able to measure its varying distance from that luminary. On the 18th of February 1842, at noon, when the sun's altitude was about  $22^\circ$ , I observed this neutral point in the most distinct manner, the polarized bands being negative below the sun, and positive near the horizon. Its distance from the sun, therefore, was about  $15^\circ$  or  $16^\circ$ . I afterwards obtained the following measures of its distance from the sun:—

	Distance of neutral point from the sun.		
1842, February 21,	<sup>h</sup>	12 39'	$15^\circ$ 0'
... April 3,		11 45	13 0
... ... 6,		11 6	12 0
... ... 8,		2 7	16 0 estimated.

On the 20th of April, in a very fine day, the wind being west and the barometer 30.02, I obtained the following measures:—

	Distance from sun.		
April 20,	<sup>h</sup>	12 10'	$11^\circ$ 20'
		12 37	10 40
		2 21	12 0
		3 45	12 35

The maximum polarization of the sky at the time of these observations was equal to a rotation of  $25\frac{1}{2}^\circ$ , about  $4\frac{1}{2}^\circ$  below the greatest maximum.

On the 26th of April 1842, when the barometer was at 30° 00', and not a cloud in the sky from morning till night\*, I obtained the following measures :—

			Distance from sun.
April 26,	<sup>h</sup>	'	
	11	1	12 15
	11	46	12 30
	3	30	14 35
	3	35	15 5
	4	10	17 45

At 10<sup>h</sup> 53', the maximum polarization of the sky, or the rotation, was 28 $\frac{3}{4}$ <sup>o</sup>, and at 11<sup>h</sup> 46', and 3<sup>h</sup> 42', it was 28 $\frac{1}{2}$ <sup>o</sup>.

On the 27th of April I observed a remarkable series of phænomena relative to this neutral point. The sky was singularly fine—the barometer at 30° 04, and at 10<sup>h</sup> 41' the maximum polarization of the sky 29 $\frac{1}{2}$ <sup>o</sup>, the greatest that I have observed. At 10<sup>h</sup> 45', the distance of the neutral point from the sun was 12° 3', and consequently about 33 $\frac{1}{2}$ <sup>o</sup> above the horizon. At 12<sup>h</sup> 12', a fog came rapidly from the sea. The neutral point below the sun was driven beneath the horizon, and Babinet's neutral point rose almost to the zenith. At 1<sup>h</sup> 20' the fog diminished. The neutral point below the sun reappeared near the horizon, oscillating up and down, through a space of 5° or 6°, as the fog became alternately denser or rarer!

When the sky is clear, the neutral point below the sun approaches to the sun as his altitude increases, and finally coincides with the sun's centre when he is in the zenith. Hence it follows, that when the sun is in the zenith, the two neutral points in his vicinity meet in the sun, and the system of polarization lines becomes uniaxal.

Were the sky sufficiently clear, we should doubtless find a secondary neutral point accompanying the primary one below the sun; but in our climate there is little chance of this phænomenon being distinctly observed.

In his observations on the antisolar *neutral point*, M. Arago observed that it sometimes deviated from the plane passing through the antisolar point and the eye of the observer; and he justly ascribed this deviation to the influence of luminous clouds situated out of this plane. The same phænomenon takes place in reference to the other neutral points, though the deviation is in these cases less distinctly seen, from the interference of the sun's light. But it is not merely the position of the neutral point that is influenced by the intrusion of

\* The lines in the spectrum were ill-defined, from unequal refraction in the air.

light different from that of the sky ; the degree of polarization is always affected whenever we measure it in parts of the sky which have luminous clouds or illuminated terrestrial objects in their vicinity, or any luminosity in the field of view of the polarimeter. If the neutral point happens to be above or below any such object, its *distance* from the antisolar point or from the sun is increased or diminished\*.

### V. On the Maximum Polarization of the Sky.

After having ascertained the position of the neutral points, or *poles of no-polarization* as we may call them, the next most important element to be determined is the *maximum polarization of the atmosphere*.

When a ray of common light is reflected from any transparent body, at an angle whose tangent is equal to the index of refraction, it is completely polarized ; or when a ray of light, completely polarized in a plane inclined  $45^\circ$  to the plane of reflexion, is reflected from any such body, its plane of polarization is brought into the plane of reflexion ; that is, *its plane is turned round  $45^\circ$* . Hence complete polarization is measured by a rotation of  $45^\circ$ . When the polarized ray is reflected at angles *above* or *below* the angle of maximum polarization, its plane is less turned round, and its rotation is more or less than  $45^\circ$ , according as the angle of reflexion is more or less distant from the angle of maximum or complete polarization†.

Different degrees of rotation below  $45^\circ$  may also be produced by the refraction of the polarized ray at one or more surfaces of glass‡, the rotation increasing with the angle of incidence. Hence we may measure the *degree of polarization* wherever it exists, by observing at what angle of incidence it is compensated or neutralized, by reflexion from a transparent surface, or by refraction at one or more such surfaces. I have found the last method the most convenient, and have therefore constructed a *polarimeter* which measures the polarization of the sky, by observing with it either the varying angle at which

\* On the 16th of May 1842, barometer 30.3, the sun was faintly seen through a thick haze. At 8<sup>h</sup> 49' A.M. the polarization was *positive* all the way from the sun to the horizon, so that the neutral point below the sun was below the horizon. Immediately afterwards the sun was quite hid—a great glare supervened, and a *quaquaversus polarization* was observed, in which the polariscope gave no coloured bands.

On the 17th of May, at 6<sup>h</sup> 30', the sun's disc was quite white through a thick haze, and there was *no neutral point either above or opposite the sun*, the polarization being everywhere *positive*. When the haze is thicker on one side of the plane passing through the sun's spectrum, the neutral point deviates from that plane.

† See Phil. Trans., 1830, p. 69.

‡ Ibid. p. 133.

it is compensated or neutralized by a fixed number of thin glass plates, or the varying number of refracting surfaces, by which the same effect may be produced at a fixed angle, capable also of being changed\*.

With a polarimeter thus constructed, I have determined that the maximum polarization of a clear blue sky is equivalent to a rotation in the plane of a polarized ray of  $30^\circ$ ; and that this maximum takes place at a distance of from  $88^\circ$  to  $92^\circ$  from the sun, and in the plane passing through the sun and the zenith. This maximum is of course dependent on the state of the atmosphere, both with respect to its magnitude and position; but we shall assume  $30^\circ$  as its amount, and  $90^\circ$  from the sun as its position in a normal state of the atmosphere, and when the sun is in the horizon.

#### VI. *On the Form of the Lines of equal Polarization in the Atmosphere.*

It is obvious, from the phænomena already described, that the polarization of the atmosphere, produced by the reflexion of the sun's light from the matter which composes the atmosphere, in planes passing through the sun, the point of reflexion, and the eye of the observer, would have been equal in circles of which the sun and the antisolar point are the centre, had there been no disturbing causes, or had the atmosphere been a perfectly transparent medium. In this case the polarization would have been complete, or  $45^\circ$ ; and this maximum would have occurred at a distance from the sun, the half of which was the polarizing angle of the medium. There is obviously, however, a cause depending on the zenith distance of the polarizing point of the sky, which acts in opposition to the polarization produced by reflexion, and compensates it at the neutral point already described. When the sun, therefore, is in the horizon, these two actions are rectangular, as in biaxal crystals; and we must therefore determine the form of the lines of equal polarization when the sun is in the horizon, and when the atmosphere is perfectly pure. When viewed, consequently, in their general aspect, the phænomena of atmospheric polarization may be represented by the formula

$$R = 30^\circ(\sin D \sin D'),$$

where  $R$  = rotation, or degree of polarization, and  $D$  and  $D'$  = the distances of the point whose polarization is required from the two neutral points.

This formula would make the lines of equal polarization

\* See the Transactions of the Royal Irish Academy, vol. xix. part 2.

*Lemniscates*, as in biaxal crystals, and consequently the polarization in the horizon greater than in the zenith, which is contrary to observation. I have therefore added a correction, depending on the zenith distance and azimuth, which makes the formula coincide better with observation, namely,

$$R = 33\frac{1}{2}^\circ (\sin D \sin D') - 6^\circ 34' (\sin Z \sin A);$$

$Z$  being the zenith distance, and  $A$  the angle of azimuth.

Assuming, therefore, that the distance of the neutral points from the sun and from the antisolar point is  $18^\circ 30'$ , when the sun is in the horizon, and that the atmosphere is perfectly pure and uniformly transparent, the lines of equal polarization will have the forms and the degrees of polarization represented by the formula. The direction of the polarization follows the same law as in biaxal crystals, the lines without bands or colour corresponding with the black hyperbolic branches in the polarized rings produced by these crystals, being distinctly seen with the polariscope.

## VII. On the Construction of the Map of the Lines of equal Polarization.

Had the map been on a greater or a less scale than it is, it might have been desirable to appropriate a single curve to every single degree, or to every two degrees of rotation or polarization. On the present scale, the curves would have been too numerous and close had there been one to each degree; and with only one to each two degrees, they would have been too distant, in so far as that the form of the curves round the neutral points would not have been sufficiently seen. I therefore adopted such a number of curves, viz.  $18\frac{1}{2}$ , as enabled me to get the curves, No. 2, continuous round each neutral point. Hence the formula became

$$N = 20.5 (\sin D \sin D') - 3.9 \sin Z \sin A,$$

or in the plane passing through the sun and the zenith, in which  $Z$  and  $A$  become zero,

$$N = 25.5 (\sin D \sin D').$$

In the zenith itself we have  $N = 18.45$ , and at  $P, P'$  we have  $N = 0$ .

The curves thus obtained do not represent values of  $N$  in degrees of rotation, but in numbers, each of which is equal to  $1^\circ 626$ . Hence  $R = N 1^\circ 626$ , and the distance between each curve is  $1^\circ 626$ . The following table contains the rotations or degrees of polarization, indicated by each of the curves numbered from  $\frac{1}{2}$  to  $18.45$  in the map :—

Values of N.	Corresponding degrees of rotation or polarization, or values of R.
$\frac{1}{2}$	0°813
1	1°626
$1\frac{1}{2}$	2°439
2	3°252
$2\frac{1}{2}$	4°065
3	4°878
4	6°504
5	8°130
6	9°756
7	11°382
8	13°008
9	14°634
10	16°260
11	17°886
12	19°511
13	21°137
14	22°764
15	24°396
16	26°016
17	27°642
18	29°268
18·45	30°000

Hence the maximum polarization of the atmosphere, as measured by a rotation of  $30^\circ$ , is equal to that produced by reflexion from a plate of glass at an angle of  $65\frac{1}{2}^\circ$ , and with a refractive index of 1·4826, or to that produced by a surface of diamond at an angle of  $75\frac{1}{2}^\circ$ . The number of refractions at a given angle, or the angle, with a given number of plates of glass, at which a rotation of  $30^\circ$  is produced, will be found from the formula in my paper on the Compensations of Polarized Light\*.

As the sun *rises* above the horizon, the lines of equal polarization change their form, and the degree of polarization varies at points of the sky whose distance from the sun is invariable. The neutral points *above* and *below* the sun approach his disc till he reaches the meridian, when the distance of each from the sun is a *minimum*; they then separate again, and attain their maximum distance, when he reaches the horizon. In countries where the sun passes across the zenith, these two neutral points coincide with the sun, when he reaches the zenith, and again separate.

\* Transactions of the Royal Irish Academy, vol. xix. part 2. p. 13.

As the sun descends beneath the horizon, the neutral point of M. Arago separates from the antisolar point, and when this point is first seen in the morning before sunrise, its distance from the antisolar point is a maximum; it gradually approaches that point till the sun rises, and also till the neutral point itself reaches the horizon, when its distance from the antisolar point is a *minimum*.

When the altitude of the sun is  $45^\circ$ , the distance  $x$  of the neutral point above the sun is about  $13^\circ 5'$ , and the distance  $x'$  of the neutral point below the sun  $6^\circ 42'$ ; at other altitudes we have

$$\begin{aligned}x &= \Delta \cos A, \\ \text{and} \quad x' &= \frac{\Delta \cos A}{\tan Z},\end{aligned}$$

$\Delta$  being  $18\frac{1}{2}^\circ$ , A the sun's altitude, and Z the zenith distance of P', the neutral point below the sun.

An interesting paper, entitled *Delle Leggi della Polarizzazione della Luce Solare nella Atmosphera Serena*, comunicato con lettera al David Brewster, LL.D., F.R.S., Lond. et Edin., membro delle Principali Accademie di Europa, del Prof. A. B. Francesco Zantedeschi, will be found in the *Raccolta Fisico-chimica Italiana*, tom. i. fascic. 10. 1846. The details in this paper are chiefly historical. The results obtained by M. Zantedeschi himself, which are of a general nature, differ in several respects from mine; but whether this difference arises from a difference in the methods of observation, or from the different states of the atmosphere under which the observations were made, I am not able to determine.

In a Memoir on the Polarization of the Atmosphere, which, I trust, will soon be published in the Transactions of the Royal Irish Academy, I shall give a full account of my observations, and enter more deeply into the subject than would have been proper in the preceding popular explanation of a Map of the Lines of Equal Polarization.

**LXIX. On the Hydrates of Nitric Acid. By MR. ARTHUR SMITH, Assistant in the Laboratory of University College, London\*.**

SOME doubt still hanging over the composition of the hydrates of nitric acid, especially of the first hydrate, I was induced to try some experiments with a view of diminishing this uncertainty. For this purpose a quantity of the red fuming acid was procured, which I examined before com-

\* Communicated by the Chemical Society; having been read June 7, 1847.

mencing my experiments very carefully for chlorine, and found to be perfectly free from that impurity, and to have a specific gravity of 1·500.

Fourteen ounces of acid of the above-named strength were mixed with 7 ounces of commercial oil of vitriol, and distilled in a sand-bath over a gas flame; the first 2 ounces that came over were rejected, and the receiver changed directly the red fumes of nitrous acid were observed to fill the interior of the retort. The acid collected was almost as dark in colour as the acid before distillation. Its specific gravity was 1·522, and it turned out to be perfectly free from the smallest trace of sulphuric acid.

I also examined the first two ounces of acid that came over very carefully for chlorine, and found it to contain scarcely a trace, nitrate of silver producing only a slight opalescence, and that which came over afterwards, being the portion that I selected for my experiments, contained none at all. This last acid, when diluted with water, gave off nitric oxide gas with a burst of effervescence, which was the principal reason why it could not be employed to ascertain the exact amount of real acid by saturation in its present dark-coloured condition.

The apparatus employed in decolorizing the nitric acid consisted of a capacious retort, capable of holding about a pint, to the beak of which was attached a large tubulated receiver, which was kept surrounded with water, to condense any little acid that might come over during the process; to the tubulure of this receiver was adapted a glass tube, bent at right angles, fitting tightly with a cork, the other extremity being in connexion with a large gas-holder, which was kept constantly filled with water, to be used as an aspirator. To the tubulure of the retort was also fitted a long glass tube bent at right angles, the one end of which terminated within an inch of its bottom, whilst the other was in connexion with a couple of tubes, each 2 feet 11 inches long, arranged side by side, and connected by means of a tube of a smaller diameter bent like the letter U.

These long tubes, through which the air was to be aspired, were filled, the one with dried chloride of calcium, and the other with pumice-stone moistened with oil of vitriol, and by these means the absence of all moisture from the air was ensured.

In decolorizing the acid a quantity amounting to 6 or 7 ounces was introduced into the retort, and after having ascertained that the whole apparatus was perfectly tight, heat was applied to the bottom of a small sand-bath in which the retort was immersed, and the temperature kept up carefully to 170° F. Then, by removing the plug at the bottom of the

gas-holder, and turning the stop-cock at the top, which was in connexion with the apparatus, a constant flow of perfectly dry air was caused to bubble through the nitric acid in the retort, the level of which was kept 2 or 3 inches above the orifice of the tube in the interior, the only passage for the air being through the long desiccating tubes. Aspiration kept up for two or three hours was found to be generally sufficient to decolorize completely 6 or 7 ounces of nitric acid.

The acid before decolorization had a specific gravity of 1.522, and after the process fell to 1.503. Fifty grs. of the colourless nitric acid were accurately weighed out in a stoppered specific gravity bottle, to which was cautiously added, whilst in the bottle, with a view to prevent any loss from splashing, a known weight of perfectly pure carbonate of soda, recently ignited in a porcelain crucible, until the solution was perfectly neutral to test-paper. The absence of any sulphate or chloride in the carbonate had been previously ascertained.

I. Carbonate of soda required 40.23 grs.

II. Carbonate of soda required 40.23 grs.

The quantity of carbonate of soda that 50 grs. of acid required for saturation, then, was 40.23 grs., which corresponds to 40.78 grs. of nitric acid, or 81.56 per cent.

An acid containing  $1\frac{1}{2}$  equiv. of water would contain in 100 parts—

Real nitric acid . . . . .	80
Water . . . . .	20
	<u>100</u>

A portion of the prepared acid, amounting to about 5 ounces, was introduced into a small retort, through the tubule of which was fitted tightly, by means of a stopping of moist clay, a delicate thermometer, which was kept immersed in the liquid. The acid began to boil at  $190^{\circ}$ , and before the distillation had come to an end it had risen to  $250^{\circ}$ . The acid coming over between  $190^{\circ}$  and  $200^{\circ}$  was collected apart to be examined by saturation.

50 grs. of the acid which remained in the retort boiling at  $250^{\circ}$  were then examined, and found to require 31.20 grs. of carbonate of soda in the first experiment, and 31.07 in the second, for saturation; the mean of the two experiments would correspond to 63.11 per cent. of nitric acid.

50 grs. of the most volatile portion, namely, that which came over between the temperatures of  $190^{\circ}$  and  $200^{\circ}$ , were then weighed out exactly; this quantity was found to require no less than 41.92 grs. in the first experiment, and 41.91 in the second, corresponding to 84.96 per cent. nitric acid; but then it must be remembered that this acid had a very dark red colour.

A quantity of this red acid was introduced into the decolorizing apparatus, and a constant rapid stream of dry air made to bubble through it for two hours; at the expiration of that time it was found to be perfectly limpid, and colourless as water, and to have a specific gravity of 1·516 at 60°.

50 grs. of the last acid were weighed out and neutralized with pure carbonate of soda as before. The numbers below will show the amount required for saturation:—

Exp. Carb. of soda. Mean.

1. . .	41·77	41·70, corresponding to 42·27, or 84·54 per cent. nitric acid.
2. . .	41·69	
3. . .	41·64	

This acid began to boil at about 184°, the greater part distilling over between the temperatures of 184° and 188°; it afterwards rose when near the end to 200°.

The first portion that came over was collected apart, introduced into the decolorizing apparatus, and dry air again drawn through it until it was quite colourless. This was found to be necessary after each distillation, on account of the decomposition that it suffered upon boiling, which rendered it as dark in colour as the original acid. 50 grs. of the colourless acid, of the specific gravity of 1·517 at 60°, were weighed out, and carbonate of soda very carefully added until neutral to test-paper. The increase in the specific gravity this time only amounted to ·001.

Exp. Carb. of soda. Acid. Mean.

1. . .	41·79	= 42·36	42·37.
2. . .	41·81	= 42·38	

Hence in 100 parts—

According to theory with 1 eq. water.

Real acid . . .	84·74	Real acid . . .	85·71
Water . . .	15·26	Water . . .	14·28
	100·00		99·99

This would give, when compared with the theoretical composition of nitric acid with 1 equiv. of water, a deficiency of ·97 in the acid, and an excess of ·98 in the water.

This hydrate, when pure, was a perfectly limpid and colourless liquid, like so much water; it boiled at 184°, and had a specific gravity of 1·517 at 60°. It was found not to have the slightest action on tin or iron even when boiled. A portion of this acid placed in a freezing mixture composed of ice and salt suffered no change.

These experiments leave little doubt concerning the composition of the first hydrate of nitric acid, namely, that it is the true mono-hydrate, consisting of 1 equiv. of nitric acid and 1 of water, HO, NO<sub>5</sub>.

*Deuto-Hydrate.*—In preparing this hydrate, I set out by obtaining a quantity of colourless strong nitric acid, the exact

amount of real acid in which was ascertained by saturation to be 79·79 per cent. To reduce this acid to the proper strength, so as to contain exactly 2 equivs. of water, it was found by calculation that it would require 63·86 grs. of water to every 1000 grs. of acid.

The proper proportions of acid and water were weighed out carefully in a stoppered specific gravity bottle, and the two mixed. This mixture was cooled down to 60° and found to have the sp. gr. 1·486.

50 grs. of this hydrate were weighed out and saturated in the usual way with recently-ignited carbonate of soda. The quantities of carbonate of soda required were as follows:—

Exp. Carb. of soda. Mean.

1. . . 37·45	}	37·49, or 74·98 per cent. acid.
2. . . 37·53		

An acid containing 2 equivs. of water will contain 75 per cent. real acid.

A portion of this acid was introduced into a small retort and distilled. It began to boil, as nearly as could be judged, at about 200°, it being difficult to come at the exact temperature on account of the very rapid rise of the thermometer, which continued to take place until it had gained the temperature of 218°; it afterwards rose when near the end to 250°.

It appears, then, from these experiments, that no such thing as a deuto-hydrate exists, but that when a mixture is made in the proportions to form such a hydrate and subjected to distillation, it divides spontaneously into the first and another, at the same time suffering considerable decomposition; and the acid which is found remaining in the retort has the exact boiling-point of the tetra-hydrate, namely, 250°; and moreover, the first portion that came over had the exact density of the first.

A portion of this acid placed in a freezing mixture of ice and salt, suffered not the least solidification.

*Tetra-Hydrate.*—This hydrate was prepared in the same way as the first, namely, by preparing a quantity of colourless acid, ascertaining its saturating power, and mixing it with the proper quantity of distilled water, ascertained by calculation. It was then tried afterwards by saturation to see if it was correct; the numbers below will show the difference:—

Exp. Carb. of soda. Acid. Mean.

1. . . 29·96 = 30·37	}	30·32, or 60·64 per cent. real acid.
2. . . 29·87 = 30·27		

According to theory with 4 eqs. water.

Real acid . . .	60·64
Water . . .	39·36
	<hr/>
	100·00

Real acid . . .	60
Water . . .	40
	<hr/>
	100

The acid had a density of 1·424 at 60°; it began to boil at 250°, and distilled over perfectly colourless and unchanged; towards the end, when slight decomposition commenced, the temperature rose to 260°.

Five or six ounces of very weak acid, of the density of 1·180, were introduced into a retort and kept heated just below its boiling-point for two or three hours; the heat was increased from time to time so as to make it boil briskly, and a thermometer introduced through the tubulure; when that which remained in the retort boiled uniformly at 250°, the heat was withdrawn and it was allowed to cool.

When the specific gravity of this acid was taken, it was found to be close upon that of the tetra-hydrate, but not exactly; probably if I had operated upon a large quantity, and carried it on for a longer time, it would have been more so; as found, its density was 1·412 instead of 1·424, which would make a difference of rather less than 1½ per cent. deficiency in the acid.

This is, I have no doubt, the proper hydrate of nitric acid, HO, NO<sub>3</sub> + 3HO, as it is generally considered; and as Dr. Dalton correctly observed, acids which are either stronger or weaker than this acid, are brought to this strength by continued ebullition, the former losing acid and the latter water.

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**LXX. On the Products of the Decomposition of Cuminate of Ammonia by Heat. By Mr. FREDERICK FIELD\*.**

THE peculiar mode of decomposition which the ammonia salts of inorganic acids exhibit when exposed to the action of heat, occurs likewise in the ammonia compounds of organic acids, although the results in the latter instances are usually of a more complicated nature. In most of these cases a formation of water takes place, the hydrogen of which is derived from the volatile alkali, while the acid furnishes the oxygen, the residue of which combines in a more intimate manner with the nitrogen of the ammonia. In decompositions, however, of *inorganic* compounds this reduction seems to be carried at once as far as it can go, the whole of the hydrogen contained in the ammonia being converted into water; while in *organic* salts this hydrogen is eliminated only by degrees, an intermediate body being produced between the original ammonia salt and the final product of the decomposition. Thus we find that nitrite and nitrate of ammonia, when exposed to heat, are at once converted into water, and respectively into nitrogen and nitrous oxide. Oxalate of ammonia,

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on the other hand, if submitted to a gentle heat, loses only two equivalents of water, the residue of both base and acid combining to form oxamide, and only by a strong and brisk application of heat Döbereiner converted it into cyanogen, the rest of the hydrogen being eliminated in the form of water.

The dry distillation of oxalate of ammonia thus affords the prototypes of two series of compounds, which may arise from ammoniacal salts by the elimination of two or four equivalents of water respectively. There are few cases, however, in which the decomposition of ammoniacal salts have been carefully studied, and the instances in which we are acquainted with the representative of the two types are exceedingly scarce. We are indeed intimate with a very great number of amidogen compounds analogous to oxamide (fumaramide, salicylamide, succinamide, anisylamide, &c.), but only few of these have been obtained from ammoniacal salts by the action of heat. The greatest number of these bodies were produced by the change most compound aethers suffer under the influence of ammonia, a beautiful mode of decomposition pointed out first by Professor Liebig in the transformation of oxalate of ethyl into oxamide, or by the action of gaseous ammonia on other substances related in some manner with the acid: thus was chloride of benzoyle converted into benzamide by Wöhler and Liebig, and lately lactide into lactimide by Pelouze.

As yet, however, the members of the second class, those compounds standing to other acids in the same relation as cyanogen to oxalic acid, are very rare. From a beautiful experiment of Pelouze, we know that the vapour of formiate of ammonia, when passed through a red-hot tube, is converted into water and hydrocyanic acid. In their investigation on the radical of benzoic acid, Wöhler and Liebig obtained a peculiar oil by the action of heat on benzamide, which at that time they did not study more closely. The same body was at a later period obtained in the dry distillation of benzoate of ammonia, and fully examined by Fehling, who found that this interesting substance, to which he gave the name *benzonitrile*, has the composition  $C_{14} H_5 N$ , and is produced from benzoate of oxide of ammonium, exactly in the same manner as cyanogen and prussic acid are formed respectively from oxalate or formiate of ammonia. These facts did not long remain isolated. Schlieper, in an excellent examination he has lately published on the products of oxidation of gelatine by chromic acid, discovered that in these reactions, among other products, the body  $C_{10} H_9 N$  is formed, valeronitryle or valerianate of ammonia—4 equivs. of water.

The members of this class acquire every day a greater degree of importance. A remarkable paper, read before the

Chemical Society a short time since by Dr. Kolbe and Mr. Frankland, has indeed opened a most interesting connexion between these bodies and another class of substances, which hitherto have been obtained by very different processes. The conversion of cyanide of ethyl into metacetonic acid by means of alkalies and acids, seems to indicate that cyanide of ethyl is nothing else than metacetonitrile. This experiment is likely to be of great importance, for it is exceedingly probable that the whole class of substances alluded to must be considered as a class of cyanogen compounds. It is evident that similar considerations may be applied to cyanide of methyl and cyanide of amyl, lately described by Balard; and the conversion of these cyanides respectively into acetic and caproic acids, which we have a right to anticipate on treating them with alkalies or acids, will prove that these compounds are the nitriles of acetic and caproic acids—acetonitrile and capronitrile—which as yet have not been obtained by the action of heat on the ammoniacal salts of these acids.

The following experiments on the action of heat on cuminate of ammonia have been made with the hope of contributing to the history of the nitriles, or organic cyanides, as they perhaps should be more correctly designated.

The cuminic acid employed in my experiments was prepared by the action of solid hydrate of potash on oil of cumin, and the product perfectly freed from the least traces of cymol which it might possibly contain by precipitating the potash salt by hydrochloric acid, dissolving the precipitated cuminic acid in ammonia, reprecipitating by hydrochloric acid, and crystallizing from water. The acid was then dissolved in strong ammonia, and the solution subjected to heat. The first portions which passed over, although consisting chiefly of water and ammonia, together with cuminate of ammonia, which is always carried over with the steam, presented more or less an opalescent appearance, indicative of traces of the oil. On evaporating the solution in the retort to dryness, a portion of the salt is decomposed, ammonia is evolved, and cuminic acid condenses in beautiful plates upon the sides and neck of the retort, separation going on even on raising the temperature; but simultaneously another decomposition takes place, water is eliminated, in consequence of which there are produced a peculiar white crystalline body, difficultly soluble in water, and subsequently a colourless oil of a most fragrant odour; although the operation may seem very simple, experience alone teaches the proper regulation of temperature necessary to obtain these two bodies.

*Cuminamide.*—Observing in my first experiments evolution of ammonia and sublimation of cuminic acid on heating cu-

minate of ammonia, I thought that by heating it under pressure, the ammonia then not being able to escape, the desired change might be effected. Accordingly a portion of the salt was placed in a strong glass tube, and after sealing the other end, gradually heated in an oil-bath to nearly the boiling-point of the oil, and allowed to cool. On cooling the mass appeared to have been completely fused, but perfectly solid and of a highly-crystallized texture. On examination it was found to be insoluble in cold water and ammonia, but very soluble in hot water, from which it solidified into a crystalline mass as the temperature cooled; this alone sufficiently indicated that a complete change had been effected, the cuminate of ammonia being readily soluble in cold water. In order to ascertain the nature of the change it was dissolved in hot water, and weak ammonia added to dissolve any cuminic acid that might be mixed with it, and crystallized; the crystals were separated by filtration, and once more dissolved in a hot weak solution of ammonia, from which they separated on cooling in brilliant white crystalline plates, similar in appearance to benzamide. These were dried at  $212^{\circ}$  in a water-bath, and analysed in the usual manner.

I. 0·174 grm. of substance burnt with oxide of copper yielded 0·470 of carbonic acid and 0·128 of water.

II. 0·248 grm. yielded 0·670 of carbonic acid and 0·181 of water.

III. To estimate the nitrogen, 0·287 grm. ignited with soda-lime yielded 0·390 of ammonio-chloride of platinum\*.

From these analytic results the following per-centages are obtained:—

	I.	II.	III.
Carbon . .	73·66	73·67	
Hydrogen . .	8·17	8·10	
Nitrogen . .			8·50

leading to the formula  $C_{20}H_{13}NO_2$ , as may be seen from the following comparison of the theoretical and experimental numbers:—

	Theory.	Mean of exp.
20 equivs. of Carbon . .	120	73·68
13 ... Hydrogen . .	13	7·99
1 ... Nitrogen . .	14	8·52
2 ... Oxygen . .	16	9·81
	163	100·00
		100·00

This body therefore is cuminamide,  $NH_2C_{20}H_{11}O_2$ , having

\* In this operation a large quantity of an oily body is produced, which floats on the surface of the hydrochloric acid. It is evidently *cumol*.

precisely the same relation to cuminate of ammonia as oxamide to oxalate of ammonia.

In preparing large quantities of this substance the employment of close tubes would be very inconvenient, and I soon found that it could be obtained in a retort by the continued application of a heat sufficient to keep the salt in a state of semi-fluidity. The analyses II. and III. were made with the product obtained in this manner.

Cuminamide crystallizes like benzamide, in two forms, according to the state of the solution ; if crystallized immediately, or from a strong solution, it separates in the form of crystalline tables of great brilliancy, but if the solution be dilute, it crystallizes after the lapse of some hours in long opake needles, both forms having exactly the same composition. It is soluble in hot and cold alcohol in any proportion, as also in aether. This new amide differs from most others that have been described in remaining intact on the addition of strong solution of potash, or mineral acids ; from the former it crystallizes in large plates after some days. Long boiling with alkalies or acids is scarcely sufficient to produce the characteristic conversion of amides either into ammoniacal salts or combinations of the base with the acid and evolution of ammonia.

*Cumonitrile.*—On heating cuminate of ammonia until it is perfectly fused, and keeping the fused mass in a state of brisk ebullition, large globules of a light yellowish oil pass over with water, evidently derived from the decomposition of the salt ; when the globules began to diminish the process was stopped, the oil was separated from the water in the receiver by means of a pipette, the remaining distillate added to the mass in the retort, and the process again repeated as before ; in this manner, after some half-dozen distillations, nearly an ounce of oil was obtained ; it was well-washed with ammonia to remove cuminic acid, which seemed to be soluble in the oil, then treated with hydrochloric acid to remove ammonia, thoroughly washed with water, and digested with chloride of calcium ; after standing some days to separate chloride of calcium, it was distilled and carefully rectified, the first portions being rejected, as possibly containing traces of water ; the middle portion was reserved and placed in a retort with a coil of platinum ; the liquid entered into ebullition at  $239^{\circ}$  C., at which point it remained stationary while at least a quarter of an ounce was passing over. This portion was employed in the following analyses :—

I. 0·212 grm. burnt with oxide of copper yielded 0·644 of carbonic acid and 0·145 of water.

II. 0·225 grm. yielded 0·6835 of carbonic acid and 0·161 of water.

III. 0·244 grm. ignited with soda-lime yielded 0·364 of ammonio-chloride of platinum\*.

From these analytical results the following per-centages are obtained :—

	I.	II.	III.
Carbon . .	82·82	82·84	
Hydrogen .	7·59	7·96	
Nitrogen .			9·34

leading to the formula  $C_{20} H_{11} N$ , as may be seen from the following comparison of the theoretical and experimental numbers :—

	Theory.	Mean of exp.
20 Carbon . .	82·76	82·83
11 Hydrogen .	7·58	7·77
1 Nitrogen .	9·66	9·34
	145	

This body is therefore cumonitrile,  $C_{20} H_{11} N$ , standing in the same relation to cuminate of ammonia as cyanogen does to oxalate of ammonia.

Cumonitrile is a perfectly clear and colourless liquid, possessing a high refractive power; it has a most powerful and agreeable odour and a burning taste; it is somewhat soluble in water, causing turbidity in that liquid; it is soluble in all proportions of alcohol and æther; it is lighter than water, having a specific gravity 0·765 at 14° C. (57° Fahr.). The boiling-point, when in contact with metal, is constant at 239° C. (462·2° Fahr.), at the barometric pressure 0·7585 m. = (29·85 inches). The equivalent of cuminic acid containing  $3C_2 H_2$  more than the equivalent of benzoic acid, it was interesting to compare the boiling-points of benzonitrile and cumonitrile. According to Fehling's experiments, the boiling-point of benzonitrile is 191° C.; on calculating from this observation the boiling-point of cumonitrile according to the rules first pointed out by Kopp, the boiling-point should be  $191 + 3\cdot19 = 248$ .

Dr. Fehling does not however mention that he had this substance in contact with metal, and it is not improbable that the true boiling-point of benzonitrile is somewhat lower; the vapour of cumonitrile is very inflammable and burns with a bright flame, which deposits much carbon.

\* Professor Fehling found it difficult to estimate the nitrogen in benzonitrile in the form of ammonia, drops of oil passing over into the hydrochloric acid. In the case of cumonitrile, this method gave very accurate results; oil drops also passed over, but they were evidently *cumol*.

The strongest nitric acid has but little action upon this substance; after boiling, however, and setting aside for some days, crystals of cuminic acid are formed. On being heated with potassium it darkened, and apparently another oil was produced; the mass on being washed and tested for cyanogen in the usual manner gave a copious precipitate of prussian blue, which seems to be strongly in favour of the view which Kolbe and Frankland have recently promulgated. A strong alcoholic solution of potash has no immediate action on cumonitrile, but after a day or two, on pouring the liquid into a watch-glass, it partially solidified into a yellow crystalline mass, a mixture of the original substance with white crystals. These crystals after purification had all the appearance of cuminamide, and in order to be satisfied of their composition—

I. 0·174 grm. burnt with oxide of copper yielded 0·472 of carbonic acid and 0·124 of water; the calculated per-centge of carbon and hydrogen from these numbers being—

Carbon . .	73·62
Hydrogen . .	7·91

These numbers correspond to those of cuminamide, as may be seen by a comparison with the former analyses.

It appears then that cumonitrile, on the addition of potash, is not, as might have been expected, converted into cuminate of ammonia, but into cuminamide, taking 2 instead of 4 atoms of water— $C_{20}H_{11}N + 2HO = C_{20}H_{13}NO_2$ , the latter body being, as before remarked, in such a remarkable degree unaffected by alkalies or acids.

Having obtained one amide with comparative ease, many other ammoniacal salts were heated for the purpose of obtaining analogous amidogen compounds. Benzoate of ammonia was tried unsuccessfully, and it appears from the account published by Fehling of his investigation of benzonitrile, that the residue in the retort consisted entirely of benzoate of ammonia, that salt appearing to have lost directly 4 equivs. of water without undergoing an intermediate conversion into an amide by the loss of 2 equivs. Nitrobenzoic acid was dissolved in ammonia, evaporated, and cautiously fused for a considerable time; when cold it was found to be insoluble in water and ammonia at the ordinary temperature, but dissolved by hot water, from which it crystallized in beautiful yellow needles. On analysis, the following results were obtained:—

I. 0·222 grm. of substance burnt with oxide of copper yielded 0·410 of carbonic acid and 0·080 of water.

II. 0·255 grm. yielded 0·472 of carbonic acid and 0·087 of water.

From these results the following per-centages were obtained:—

	I.	II.
Carbon . . .	50·36	50·43
Hydrogen . .	4·00	3·78

corresponding to the formula  $C_{14}H_6N_2O_6$ , as may be seen from the comparison of the theoretical and experimental numbers:—

	Theory.	Mean of exp.
14 equivs. of Carbon . .	84	50·60
6 ... Hydrogen . .	6	3·62
2 ... Nitrogen . .	28	16·87
6 ... Oxygen . .	48	28·91
	<u>166</u>	<u>100·00</u>

This body is therefore nitrobenzamide, having the same relation to nitrobenzoate of ammonia as cuminamide has to cuminate of ammonia.

This beautiful substance can only be obtained with difficulty, as the nitrobenzoate of ammonia explodes violently unless very great caution is employed.

A specimen of chlorobenzoic acid, made in the laboratory for some other investigation, was dissolved in ammonia and heated; it fused readily, became perfectly insoluble in cold water and ammonia, but soluble in hot water, crystallizing as the solution cooled in long needles of great beauty. The specimen of acid afforded me, being all that could be spared, was insufficient for the manufacture of an amide; I prepared a portion of chlorobenzoic acid by acting upon benzoic acid for some days with hydrochloric acid and chlorate of potash; after purification it was burnt with chromate of lead and gave the following results:—

I. 0·394 grm.=0·769 of carbonic acid and 0·114 of water.

From this result the following per-centages were obtained:—

	Experiment.	Theory.
Carbon . . .	53·22	53·61
Hydrogen . .	3·22	3·25

leading to the formula  $HO, C_{14} \left\{ \begin{matrix} H_4 \\ Cl \end{matrix} \right\} O_3$ , 1 equiv. of the hydrogen of benzoic acid replaced by an equivalent of chlorine.

This acid, however, on being subjected to the usual treatment by solution in ammonia and subsequent heat, did not fuse but blackened, charcoal being separated. Unfortunately the specimen of ammoniacal salt from which I had made the former compound was not analysed, probably it would have

proved to be  $C_{14} \left\{ \begin{matrix} H_3 \\ Cl_2 \end{matrix} \right\} O_3$ , HO, or  $C_{14} \left\{ \begin{matrix} H_2 \\ Cl_3 \end{matrix} \right\} O_3$ , HO, a dichlorobenzoic or a trichlorobenzoic acid, such existing.

These experiments were conducted in the laboratories of the Royal College of Chemistry under the direction of Dr. Hofmann, to whom I beg to offer my best thanks for his advice and assistance during their progress.

**LXXI.** *On the General Solution (in certain cases) of the equation  $x^3 + y^3 + Az^3 = Mxyz$ , &c. By J. J. SYLVESTER, A.M., F.R.S., late Professor of Natural Philosophy in University College, London\**.

I SHALL restrict the enunciation of the proposition I am about to advance to much narrower limits than I believe are necessary to the truth, with a view to avoid making any statement which I may hereafter have occasion to modify. Let us then suppose in the equation

$$x^3 + y^3 + Az^3 = Mxyz$$

that  $A$  is a *prime* number, and that  $27A - M^3$  is *positive*, but exempt from positive prime factors of the form  $6i + 1$ . Then I say, and have succeeded in demonstrating, that all the possible solutions in integer numbers of the given equation may be obtained by explicit processes from one particular solution or system of values of  $x, y, z$ , which may be called the Primitive system.

This system of roots or of values of  $x, y, z$  is that system in which the value of the greatest of the three terms  $x, y, A^{\frac{1}{3}}z$  (which may be called the Dominant) is the least possible of all such dominants. I believe that in general the system of the least *Dominant* is identical with the system of the least *Content*, meaning by the latter term the product of the three terms out of which the *Dominant* is elected. I proceed to show the law of derivation.

To express this simply, I must premise that I shall have to employ such an expression as  $S' = \phi(S)$  to indicate, not that a certain quantity,  $S'$ , is a function of  $S$ , but that a certain system of quantities disconnected from one another, denoted by  $S'$ , are severally functions of a certain other system of quantities denoted by  $S$ ; and, as usual, I shall denote  $\phi\phi S$  by  $\phi^2S$ ,  $\phi\phi^2S$  by  $\phi^3S$ , and so forth.

Let now  $P$  be the Primitive system of solution of the equation

$$x^3 + y^3 + Az^3 = Mxyz,$$

\* Communicated by the Author.

$P$  denoting a certain system of values of and written in the order of the letters  $x, y, z$ , which may always be found by a limited number of trials (provided that the equation admits of any solution). That this is the case is obvious, since we have only to give the Dominant every possible value from the integer next greatest to  $A^{\frac{1}{3}}$  upwards, and combine the values of  $x^3, y^3, Az^3$  so that none shall ever exceed at each step the cube of such dominant, and we must at last, if there *exist any solution*, arrive at the System of the Least Dominant.

Now, every system of solution is of one or the other of two characters. Either  $x$  and  $y$  must be odd and  $z$  even, or  $x$  and  $y$  must be one odd and the other even and  $z$  odd. That all three should be odd is inconsistent with the given conditions as to  $A$  being odd and  $M$  even; and if all three were even, by driving out the common factor we should revert to one or the other of the foregoing cases.

The systems of solution where  $z$  is even may be termed Reducible, those where  $z$  is odd Irreducible. Let  $\varphi$  denote a certain symbol of transformation hereafter to be explained.

Then the Reducible systems of the first order may be expressed by

$$\varphi P, \varphi^2 P, \varphi^3 P, ad infinitum;$$

or in general by  $\varphi^{n_1} P$ ,  $n_1$  being absolutely arbitrary. I will anticipate by stating that the function  $\varphi$  involves no *variable* constants; that is to say,  $\varphi(S)$  may be found explicitly from  $S$  without any reference to the particular equation to which  $S$  belongs. Let now  $\psi$  denote another symbol of transformation, also hereafter to be defined, and differing from  $\varphi$  insofar as it does involve as *constants* the three values of  $x, y, z$  contained in  $P$ : then the general representations of Irreducible systems of the first order will be denoted by  $\psi \varphi^{n_1} P$ .

It is proper to state here that the symbol  $\psi$  is ambiguous; and  $\psi \varphi^{n_1} P$ , when  $P$  and  $n_1$  are given, will have two values, according to the way in which the terms represented by  $P$  are compared with  $x, y, z$  in the given equation

$$x^3 + y^3 + Az^3 = Mxyz;$$

for it is obvious that if  $x=a, y=b, z=c$  satisfies the equation, so likewise will

$$x=b, y=a, z=c.$$

Each however of these values of  $\psi \varphi^{n_1} P$  gives a solution of the kind above designated.

Proceeding in like manner as before, the Reducible system of the second order may be designated by  $\varphi^{n_2} \cdot \psi \varphi^{n_1} P$ , the Irreducible by  $\psi \varphi^{n_2} \cdot \psi \varphi^{n_1} P$ ; and in general *every possible*

system of values of  $x, y, z$  satisfying the proposed equation, in which  $z$  is even, is comprised under the form

$$\phi^{n_r} \cdot \psi \phi^{n_{r-1}} \cdot \psi \dots \phi^{n_2} \cdot \psi \phi^{n_1} \cdot P;$$

and every possible system of such values, in which  $z$  is odd, is comprised under the form

$$\psi \phi^{n_r} \cdot \psi \phi^{n_{r-1}} \cdot \psi \dots \psi \phi^{n_1} \cdot P;$$

the quantities  $n_1 n_2 \dots n_r$  being of course all independent of one another, and unlimited in number and value.

Thus then we may be said to have the general solution of the given equation in the same sense as an arbitrary sum of terms, each of a certain form, is in certain cases accepted as the complete solution of a partial differential equation.

As regards the value of the symbols  $\psi$  and  $\phi$ ,  $\phi$  indicates the process by which  $a, b, c$  becomes transformed into  $\alpha, \beta, \gamma$ , the relations between the two sets of elements being contained in the following equations :

$$a' = a^3 \quad b' = b^3 \quad c' = Ac^3$$

$$\alpha = a'^2 \quad b' + b'^2 \quad c' + c'^2 - 3a'b'c'$$

$$\beta = a' \quad b'^2 + b' \quad c'^2 + c'a'^2 - 3a'b'c'$$

$$\gamma = abc\{a'^2 + b'^2 + c'^2 - a'b' - a'c' - b'c'\}.$$

Next, as to the effect of the Duplex symbol  $\psi$ . Let  $e, g$  be the elements of the Primitive system  $P$ :  $i$  being the value of  $z$  and  $e, g$  of  $x$  and  $y$  taken in either mode of combination, each with each, which satisfy the proposed equation

$$x^3 + y^3 + Az^3 = Mxyz.$$

Let  $l, m, n$  represent any system  $S$ ,

$\lambda, \mu, \nu$  represent any system  $\psi(S)$ ,

$\psi S$  has two values, which we may denote by  $\psi' S$ ,  $'\psi S$  respectively, and accentuating the elements  $\lambda, \mu, \nu$  accordingly to correspond, we shall have

$$\lambda' = 3gm(gl - em) + 3Am(il - en) - M(gil^2 - e^2lm)$$

$$\mu' = 3Am(im - gl) + 3el(em - gl) - M(eim^2 - g^2lm)$$

$$\nu' = 3el(en - il) + 3gm(gn - im) - M(egn^2 - i^2lm) :$$

we have then

$$\psi \cdot S \equiv \lambda', \mu', \nu',$$

and in like manner

$$'\psi S \equiv \lambda', \mu', \nu,$$

$'\psi S$  being derived from  $\psi S$  by the mere interchange of  $e$  and  $g$  one with the other.

I have stated that every possible solution of the proposed equation comes under one or the other of the orders, infinite

in number and infinite to the power of infinity in variety of degree, above given: this is not strictly true, unless we understand that all systems of solution are considered to be equivalent which differ only in a multiplier common to all three terms of each; that is to say, which may be rendered identical by the expulsion of a common factor. So that  $m\alpha, m\beta, m\gamma$  as a system is treated as identical with  $\alpha, \beta, \gamma$ , which of course substantially it is; and it should be remarked that there is nothing to prevent the operations denoted by  $\phi$  and  $\psi$  introducing a common factor into the systems which they serve to generate, and the latter in particular will have a strong tendency so to do.

I believe that this theorem may be extended with scarcely any modification to the case where  $A$ , instead of being a prime, is any power of the same, and to suppositions still more general. I believe also that, subject to certain very limited restrictions, the theorem *may* prove to apply to the case where the determinant  $27A - M^3$  becomes negative.

The peculiarity of this case which distinguishes it from the former, is that it admits of all the three variables  $x, y, z$  in the equation

$$x^3+y^3+Az^3=Mxyz$$

having the same sign, which is impossible when the determinant is positive; or in other words, the curve of the third degree represented by the equation  $Y^3+X^3+1=\frac{M}{A^{\frac{1}{3}}}XY$  (in which I call the coefficient of  $XY$  the characteristic), which, as long as the quantity last named is less than 3, is a single continuous curve extending on both sides to infinity, as soon as the characteristic becomes equal to 3 assumes to itself an isolated point, the germ of an oval or closed branch, which continues to swell out (always lying apart from the infinite branch) as the characteristic continues indefinitely to increase.

I ought not to omit to call attention to the fact that the theorem above detailed is always applicable to the case of the equation

$$x^3+y^3+Az^3=0,$$

when  $A$  is *any* power of a prime number *not* of the form  $6i+1$ ; in other words, the above always belongs to the class of equations having Monogenous solutions, which for the sake of brevity may be termed themselves Monogenous Equations\*.

\* Thus the equation  $x^3+y^3+Az^3=0$  alluded to by Legende is Monogenous, and the Primitive system of solution is  $x=1 y=2 z=-1$ , from which every other possible solution in Integers may be deduced.

On the probable existence of such a class of equations I hazarded a conjecture at the conclusion of my last communication to this Magazine. As I hope shortly to bring out a paper on this subject in a more complete form, I shall content myself at this time with merely stating a theorem of much importance to the completion of the theory of insoluble and of Monogenous equations of the third degree; to wit, that the equation in integers

$$a(x^3+y^3+z^3)+c(x^2y+y^2z+z^2x+xy^2+yz^2+zx^2)+exyz=0$$

may always be transformed so as to depend upon the equation

$$fu^3+gv^3+hw^3=(6a-e)uvw,$$

wherein  $fgh = ae^2 - (c^2 + 3a^2)e + 9a^2 - 3ac^2 - 2c^3$ .

By means of the above theorem, among other and more remarkable consequences, we are enabled to give a theory of the irresoluble and monogenous cases of the equation

$$x^3+y^3+m^3z^3=Mxyz,$$

when  $m$  is some power of 2, or of certain other numbers.

26 Lincoln's Inn Fields,  
Nov. 17, 1847.

J. J. S.

**ERRATUM.**—In the October Number, at page 295, a little below the middle, for  $y=117949000$  read the same with the number 1 added at the end. At page 293, last line, omit the words after “provided” as far as “divisible by 9” on the following page, and read in lieu, “provided in the second case that ABC is of the form  $9m+1$  and that D is divisible by 9.”

## LXXII. *On Cochineal (Coccus Cacti). First Memoir.* By WARREN DE LA RUE, Esq.\*

THE beautiful theoretical results which have been lately obtained by a closer examination of indigo blue and its products of decomposition, made it desirable to undertake similar investigations with other colouring matters. I made choice of the colouring principle of cochineal (*Coccus Cacti*), hoping that a detailed research might not only prove of interest in a scientific point of view, but also throw some light on its practical applications, and the more so, as the recent investigations of Preisser had seemed to point out a very close

\* Communicated by the Chemical Society; having been read June 21, 1847.

analogy in the chemical properties of a variety of colouring matters with indigo blue.

Before entering into the detail of my experiments, I think it desirable to give a brief outline of the results obtained by the chemists who have hitherto worked on this subject.

Dr. Jean Frédéric John, in a quarto volume translated from the German and entitled *Tableaux Chimiques du Règne Animal*, appears to have published the first analysis of cochineal: he does not describe his method, but merely states that it contains the following per-centage:—

Colouring principle (semi-solid, soluble in water and alcohol) . . . . .	} 50·00
Gelatine . . . . .	10·50
Waxy fat . . . . .	10·00
Modified mucus . . . . .	14·00
Membrane . . . . .	14·00
Alkaline phosphates and chlorides, phos- phate of lime, phosphate of iron, and phosphate of ammonia . . . . .	1·50
	<hr/>
	100·00

Pelletier\* and Caventou, in a very long memoir read before the Institut de France in 1818, have gone very elaborately into the examination of cochineal and obtained many interesting results. In analysing this substance they employed the following process:—They removed the fatty bodies by boiling æther, in which they found the colouring matter but slightly soluble; these fatty substances, recovered by distilling off the æther, were considered to consist of stearine, oleine, and an aromatic acid, from which latter substance it was difficult to remove the adhering colouring matter.

The cochineal, exhausted with æther, was treated with alcohol of 40° Beaumé, which dissolved the colouring matter, together with a small quantity of fatty and nitrogenous substances.

On cooling, and by spontaneous evaporation, they obtained a granular red residue of a semi-crystalline appearance, and which they considered to be the colouring matter contaminated still with nitrogenous matter (*matière animalisée*) and some fatty bodies, the greater part of which remained undisolved in strong cold alcohol; by repeating the operation once or twice they considered that the substance was obtained almost in a state of purity. To remove the last traces

\* *Annales de Chimie et de Physique*, sér. 2, tome viii. p. 250. *Journal de Pharmacie*, sér. 2, tome iv. p. 193.

of foreign matter it was dissolved in strong alcohol, and an equal volume of æther added, which precipitated the colouring matter and retained the fat, which was still adhering to it. The colouring matter thus purified they named carmine (*carminium*), and described as being very soluble in water, from which it did not crystallize, more or less soluble in alcohol, according to its strength, and quite insoluble in æther and the fixed and volatile oils. Acids did not precipitate it from its aqueous solution if free from animal matter. They found hydrochloric and sulphuric acid to decompose it; the latter with elimination of carbon. By the action of nitric acid they obtained an acid in prismatic crystals resembling oxalic acid, but differing in some of its properties.

On heating the "carmine" it intumesced and gave off carburetted hydrogen, a considerable quantity of oily substances, a little acid water, but no trace of ammonia. Chlorine and iodine decomposed it; the alkalies in the commencement produced merely a change in colour, turning it violet, but by the assistance of time or heat they effected a complete alteration. They found an aqueous solution of "carmine" to exhibit the following comportment with reagents.

Of the alkaline earths, lime only produced a precipitate; hydrate of alumina showed a marked affinity, absorbing the whole of the colouring matter from an aqueous as well as an alcoholic solution; the presence of alum prevented this reaction: iron, copper, and silver salts were without reactions; terchloride of gold destroyed the colour; neutral salts of lead merely changed it to violet, except the neutral acetate, which precipitated it, the free acetic acid retaining a little of the compound in solution; the colouring matter could be recovered by decomposing the lead compound with hydrosulphuric acid. The nitrate of mercury gave a purple, and the pernitrate a scarlet-red precipitate; the bichloride no precipitate; chloride of tin gave a violet precipitate; the bichloride changed the colour to scarlet without causing a precipitate. Albumen and gelatine had no marked action, but if precipitated by reagents the colouring matter was carried down.

In a later communication (1832), Pelletier\* gave the composition of the colouring matter as prepared by himself and Caventou. In a previous qualitative examination they had failed to exhibit the presence of nitrogen which M. Pelletier now detected. The substance was dried *in vacuo* at a gentle heat to remove every trace of alcohol and æther, and burnt with oxide of copper it yielded—

\* *Annales de Chimie et de Physique*, sér. 2, tome li. p. 194.

Carbon . . . . .	49.33
Hydrogen . . . . .	6.66
Nitrogen . . . . .	3.56
Oxygen . . . . .	40.45
	<hr/>
	100.00

M. Pelletier stated, however, that he did not greatly rely on the correctness of this analysis.

After alcohol had dissolved out all the colouring matter removable by it, they extracted the last traces, by repeatedly washing the residue with boiling water, and along with it a little fatty and some nitrogenous matter; the residue was a brownish transparent mass. The later decoctions, containing no red colouring matter, left likewise on evaporation a brownish transparent mass, which they considered identical with the organic residue of the insect. This animal matter had, according to them, some analogy with gelatine, but differed in many of its properties, as it did also from albumen and fibrine, they therefore considered it as peculiar to the cochineal insect; the alkalies and ammonia dissolved it readily; chlorine precipitated it; all acids and acid salts precipitated it, as also acetate of lead, salts of tin and copper, and nitrate of silver; and they considered the latter reagent as a good test of the purity of the colouring matter, as it did not precipitate the latter if free from nitrogenous substances. If the colouring matter were contaminated with nitrogenous substances, all the salts which precipitated the latter carried down likewise some of the colouring matter.

An examination of the ashes showed the presence of phosphate of lime, carbonate of lime, chloride of potassium, and phosphate of potash, to the extent of 0.7 per cent.

In the second part of the memoir they went into the theory of the technical applications of the colouring matter: this having no reference to the present subject, I do not think it necessary to reproduce it here.

M. Lassaigne, in 1819\*, examined Kermes (*Coccus ilicis*), an insect common in the South of Europe, and employed as a red dye before the discovery of America, and obtained by following the methods of Pelletier and Caventou, substances agreeing in their properties with the analogous ones found in cochineal.

M. F. Preisser†, in an elaborate paper on the origin and nature of colouring matters, has again drawn the attention of chemists to the subject. This gentleman, from a study of a variety of colouring substances, comes to the conclusion that all resemble indigo in its behaviour with reducing agents.

\* *Journal de Pharmacie*, sér. 2, tome v. p. 435.

† *Ibid.* p. 191.

He affirms that he obtained by the action of hydrosulphuric acid on the lead compounds of a great number of organic colouring matters, substances bearing the same relation to the original colouring matters as white indigo does to blue indigo. In order to obtain the colourless modification of the colouring matter of cochineal, he adds what he terms "hydrate of oxide of lead" to an aqueous decoction of cochineal, the fats being previously removed by æther. The colouring matter is entirely removed by the so-called oxide of lead, which is nothing but a basic nitrate of lead,  $2(3\text{PbO}, \text{NO}_5) + 3\text{HO}$ . The lead compound suspended in water (hot?) was decomposed by a stream of hydrosulphuric acid; the nearly colourless filtrate deposited on cooling needles of a pale yellow colour, which became perfectly white by washing with æther and pressing between bibulous paper; these crystals, which, according to his statement, are soluble in water and alcohol, but less so in æther, assume in contact with the atmosphere the purple-red of the colouring matter of cochineal. He moreover asserts that his colourless modification gives a white lead salt on adding acetate of lead to its aqueous solution, and that this assumes a purple colour in contact with the air.

He proposes to give the name carmine, hitherto applied to the red colouring matter, to the white crystals, and to designate the red substance by the name "Carméine."

The statements of Preisser, generalizing most beautifully under one head the chemical character of all colouring matters, making indigo as it were the prototype of them all, could but induce other chemists to work out more in detail the relations cursorily pointed out in the memoir of this chemist. Unfortunately a careful repetition of these experiments has not confirmed the basis on which his theory reposes.

M. A. E. Arppe repeated Preisser's experiments on the colouring matter of cochineal\*. He found that by proceeding in the manner described by Preisser that he could only obtain a red solution, which on evaporation was converted into white crystals of oxalic acid by the nitric acid derived from the basic lead salt.

Arppe now prepared a pure oxide of lead by precipitating acetate of lead with potash. He found that this would not take down the colouring matter in the cold, but by boiling it is carried down as a blue lake, which he decomposed by hydrosulphuric acid; the supernatant liquor was nearly colourless, the colouring matter he found adhered with great obstinacy to the sulphuret of lead, from which water, alcohol and ammonia failed to separate it; but sulphuret of ammo-

\* Liebig's *Annalen*, vol. lv. p. 101.

nium and acids rendered it perceptible. He likewise tried to obtain the colouring matter in a state of purity by precipitating with hydrated oxide of lead an aqueous decoction of cochineal (previously purified from nitrogenous substances by nitrate of silver). On treating the precipitate by hydrosulphuric acid, he obtained a red liquor of *strongly acid reaction*, the acid of which was not derived from the lead salt: on evaporation it left a dark red mass, emitting the smell of burnt sugar. Wishing to separate the acid, which he thought contaminated the colouring matter, he prepared a strong aqueous decoction of cochineal, and after separating the nitrogenous matter by means of nitrate of silver, filtering, and then saturating by ammonia, and afterwards adding the hydrated oxide of lead, he found that the supernatant ammoniacal liquor, which was nearly colourless, yielded by evaporation an acid liquid; and on decomposing the lead lake with hydrosulphuric acid, he obtained a liquid slightly coloured (the colouring matter adhering to the sulphuret of lead), which was likewise acid. From this he concluded that the colouring matter had not up to that period been obtained in a state of purity.

#### *Microscopic Examination of Living Cochineal.*

By the kindness of Sir James Clark, who furnished me with specimens of the living insect, I have been enabled to examine the physical characters of the colouring matter as it exists in the organism of this little insect before it is subjected to the process of drying for commerce. On examination by the microscope, the white dust which covers the insect and the adjacent parts of the cactus leaves, on which it feeds, has all the characters of an excrement; it has a curled cylindrical form, is of very uniform diameter and of a white colour. On removing the powder with a little æther and piercing the side of the little creature, a quantity of a purplish red fluid exudes, which contains the colouring matter in minute granules assembled round a colourless and larger nucleus, and these groups float in a colourless fluid. It is evident from this, that, whatever may be the function of the colouring matter, it has a distinct and marked form, and does not pervade as a mere tint the fluid portion of the insect.

#### *Separation of the Colouring Matter.*

It became evident from a few preliminary experiments that the investigation would be greatly facilitated by the employment of a large quantity of material; and as in the course of the inquiry different methods were adopted for the prepara-

tion of the colouring matter, capital letters will be used to designate the various preparations.

A. About 3 lbs. of ground cochineal (technically known as shelly black) was introduced into 15 gallons of boiling distilled water, and the mixture maintained at that temperature for twenty minutes; the decoction, strained through a sieve, was allowed to subside for a quarter of an hour and then decanted off; whilst still hot the transparent liquid was mixed with basic nitrate of lead, added with caution to avoid excess; a fine purple lake was thus obtained, the supernatant liquor retaining only a pale buff tinge. After decantation of the supernatant liquor, the lake was thrown on a cloth filter and washed with distilled water until the filtrate gave but a slight opalescence with chloride of mercury, which was found to be a test for the presence of nitrogenous matter. The lead lake was then suspended in distilled water and treated with a copious stream of hydrosulphuric acid, when a precipitate of sulphuret of lead and a deep red supernatant liquid was obtained; on stirring the liquid this colour almost disappeared, the colouring matter being evidently absorbed by the sulphuret, agreeing perfectly with Arppe's observation. A fresh stream of gas reproduced the colour, which was again absorbed on stirring; after continuous treatment with hydrosulphuric acid, the lead lake being completely decomposed, the filtered liquid was evaporated in a water-bath to a syrupy consistence, and the evaporation finished as far as possible at a temperature of 38° C. The semi-solid substance thus obtained was of a deep purple colour, had a strongly acid reaction, and evolved the smell of burnt sugar, as noticed by Arppe. The weight of this substance, which I call crude carminic acid, was 3½ ozs., and 1 oz. more was obtained from the residue by similar treatment.

B. On repeating the same process the whole product was lost. An excess of the basic nitrate having been employed, the nitric acid set free by the hydrosulphuric acid caused a violent decomposition, with evolution of nitrous fumes, as soon as the carminic acid arrived at a pasty consistence; this agrees also with Arppe's experience.

C. In this operation a decoction of cochineal, made in the described manner, was precipitated with a solution of acetate of lead acidulated with acetic acid (six parts by weight of crystallized acetate, and one part of strong acetic acid). The resulting lead lake, being very bulky, was washed by decantation with boiling distilled water, collected on a filter, dried in a current of warm air, and finely powdered; 17 ozs. of *crude carminate of lead* were thus obtained.

D. Half a pound of cochineal was boiled with five pints of alcohol, spec. grav. .830. The filtered tincture deposited on cooling a granular precipitate, consisting chiefly of fatty matter retaining a portion of colouring matter; on concentrating the tincture by distillation a further quantity was deposited, which was filtered off; the filtrate was evaporated to dryness *in vacuo*, when after eight weeks a gummy residue was obtained. This mass dissolved with great difficulty in a large quantity of absolute alcohol, a red flocculent substance consisting chiefly of nitrogenous matter remaining undissolved. The alcoholic solution filtered off from this deposit, concentrated by distillation and finally evaporated *in vacuo* over sulphuric acid, dried to a tenacious semi-solid mass, covered with a colourless oily fluid, and containing crystalline particles of a solid fat. After removal of the fats by means of æther, this mass was digested in water at 38° C., which partly dissolved it with a fine red colour, leaving a brown mass of resinous aspect behind, more of which deposited on the cooling of the coloured liquid; the decoction was now evaporated to the consistence of a syrup, and finally dried *in vacuo* over sulphuric acid.

These are all the processes employed to *extract* the colouring matter from the cochineal; I may here remark, before entering on the details of its further purification, that I obtained other substances on evaporating the mother-liquors from which the colouring matter had been separated by lead salts, which will be hereafter described.

*Purification of the Carminic Acid.*—In my first attempts to purify the colouring matter I proceeded in the following way:—An aqueous solution of the crude carminic acid (A) was precipitated with acetate of lead, the precipitate of carminate of lead well-washed and decomposed by hydrosulphuric acid; the red supernatant liquid was first concentrated on the water-bath and finally dried *in vacuo*; a highly hygroscopic purple residue was thus obtained.

I could not, by whatever means I adopted, effect the decolorization of the colouring principle. In several attempts I heated the solution for some hours to 100° C., keeping up a continuous current of hydrosulphuric acid, and in other experiments a stream was made to pass for several days through the disengaged colouring matter, but without the slightest change in its aspect. From these experiments, made with the greatest care and at several periods, I am led to the same conclusion as Arppe, that Preisser must have been mistaken in his results, and I regret that I cannot throw any light on the probable cause of his error.

Several combustions of the carminic acid thus purified were made, the resulting numbers however became useless by the subsequent observation that this acid was by no means pure. A sufficient quantity being incinerated left a residue of acid reaction, which was suspected to contain phosphoric acid. Carminic acid burning only with great difficulty, it was reconverted into carminate of lead, the oxide of lead dissolved out of the residue obtained after fuming by acetic acid, which left a white residue of metaphosphate of lead, together with a little lead. The white residue was soluble in dilute nitric acid, and exhibited, when treated before the blowpipe, the characters of metaphosphate of lead; other tests likewise confirmed the presence of phosphoric acid. It will hereafter be seen that the process of extracting the colouring matter by alcohol (D) does not exclude the phosphoric acid, which in all probability existed in the colouring matter analysed by Pelletier. It is further evident that the presence of phosphoric acid explains most satisfactorily the facts observed by Arppe.

a. In order to separate the phosphoric acid, another portion of crude carminic acid (A) was precipitated with acetate of lead. Three-fourths of the carminate of lead produced were decomposed by hydrosulphuric acid and evaporated to dryness in the way already mentioned. The dry mass being dissolved in cold absolute alcohol, and filtered from a slight flocculent brownish residue, was heated to ebullition in a water-bath and mixed with the remaining fourth of the carminate of lead, which had been previously reduced to a fine powder; the ebullition was continued for a few hours. In this method the free phosphoric acid combined with the lead, liberating an equivalent proportion of carminic acid, which was taken up by the alcohol. The alcoholic solution was filtered whilst hot, concentrated by distillation, and then evaporated *in vacuo* in the presence of sulphuric acid; it dried into a granular mass of a deep purple-brown colour, detaching itself spontaneously from the sides of the vessel, and on examination by the microscope was found to be a beautiful transparent crimson substance, exhibiting only slight, if any, signs of crystalline structure; by pulverization it became of a fine scarlet colour; it left a mere trace of ash, and was found to be perfectly free from phosphoric acid. It was highly hygroscopic.\*

\* In consequence of this it was found convenient to dry the carminic acid intended for analysis in little stoppered tubes in the air-pump, as the stopper could be rapidly inserted after desiccation, and access of air effectually prevented.

Burnt with chromate of lead,—

I. ·4647 grm. gave ·9096 grm. carbonic acid and ·2175 grm. water.

II. ·4630 grm. gave ·9105 grm. carbonic acid and ·2140 grm. water.

For the latter analysis I am indebted to my friend Mr. Nicholson.

b. A second preparation of carminic acid was made by operating on the crude carminate of lead (C) and treating the resulting crude carminic acid in the manner just described for the preparation a. It left on incineration 0·2 per cent. of ash (·1609 grm. giving ·0003 grm. ash), which was neglected in the following analyses:—

III. ·3710 grm. gave ·7316 grm. carbonic acid and ·1710 grm. water.

IV. ·3685 grm. gave ·7235 grm. carbonic acid and ·1722 grm. water.

c. To effect the purification of the carminic acid (D) obtained by digesting cochineal in alcohol, it was dissolved in water and precipitated by acetate of lead; the filtrate was found to contain nitrogenous matter, and the carminate of lead to be contaminated with phosphate of lead; it was therefore treated in the manner already detailed.

V. ·3925 grm. of this substance gave ·7658 grm. carbonic acid and ·1780 grm. water.

d. A fourth preparation of carminic acid was obtained by substituting phosphoric acid for hydrosulphuric in the decomposition of the crude carminate of lead (C), and evaporating the carminic acid to dryness in contact with a fresh portion of carminate of lead; this did not however separate entirely the phosphoric acid, it was therefore redissolved in boiling absolute alcohol, and maintained some time at that temperature with more carminate of lead. On analysis—

VI. ·3805 grm. gave ·7530 grm. carbonic acid and ·1848 grm. water.

Pelletier having obtained in his analysis of "carmine" (carminic acid) as much as 3·56 per cent. of nitrogen, all the before-cited preparations of carminic acid were carefully examined qualitatively for nitrogen by heating with soda-lime, and without exception gave indications of its presence; in most cases but a mere trace was found, but I thought it necessary notwithstanding to make a few quantitative determinations, especially as M. Berzelius\* had pointed out the improbability of it being an essential constituent.

\* *Traité de Chim.* t. iii. p. 808. Brussels, edit. 1839.

The last preparation (*d*) appearing to contain more than any of the others, it was chosen and burnt with soda-lime.

It was indispensable in experiments of this nature to test the purity of the soda-lime as regarded the absence of ammonia. A tube having 9 inches of its length filled with soda-lime was heated to redness, just as in a nitrogen determination ; the hydrochloric acid, being treated with bichloride of platinum in the usual manner, gave 7.5 milligrammes of ammonio-chloride of platinum ; and a repetition of the experiment gave a similar result. This allowance has been made on all the nitrogen determinations by soda-lime.

·5938 grm. carminic acid (*d*) gave ·0717 grm. ammonio-chloride of platinum = 0.76 per cent. of nitrogen.

This quantity of nitrogen could not be supposed to belong to the composition of the colouring matter, but was evidently due to some foreign substance, and not improbably to ammonia. In order to purify the carminic acid still more, the same specimen (*d*) was dissolved in a small quantity of boiling absolute alcohol and the filtered solution mixed with three times its bulk of anhydrous æther ; a splendid scarlet precipitate was immediately produced, which absorbed water rapidly from the atmosphere, and agglutinated into a dark purple mass ; when dried it weighed 0.3 grm. (*e*). The filtrate, which was of a pale orange-red colour, left on evaporation 0.5 grm. of carminic acid (*f*).

·2635 grm. (*e*) burnt with soda-lime gave ·0637 grm. ammonio-chloride of platinum = 1.52 per cent. of nitrogen.

·4732 grm. (*f*) gave ·0150 grm. ammonio-chloride of platinum = 0.2 per cent. of nitrogen.

We have therefore (*e*) 0.3 grm. found to contain by analysis 1.5 per cent. nitrogen, and (*f*) 0.5 grm. 0.2 per cent.,  $\frac{(3 \times 1.5) + (5 \times 0.2)}{8} = .69$  average per cent., which agrees

closely with ·76, found previous to treatment with æther.

*g.* Another preparation of carminic acid was obtained by precipitating crude carminic acid with acidulated acetate of copper, which salt was found to carry down the carminic acid, and to leave in solution by far the greater portion of the phosphoric acid. The carminate of copper, which occupied a long time in washing, was collected and decomposed by hydrosulphuric acid. The filtrate was evaporated to dryness, dissolved in boiling absolute alcohol, filtered, concentrated by distillation, and again evaporated to dryness *in vacuo*. It still contained a trace of phosphoric acid. On evaporating the mother-liquor and filtering, from an impure carminate of copper which deposited as the acetic acid was driven off, and

again concentrating to dryness, a brown mass was obtained, which on incineration left a greenish-white very hygrometric ash, in which phosphoric acid, soda and copper were found. Burnt with chromate of lead—

VII. ·4020 grm. carminic acid (*g*) gave ·7842 grm. carbonic acid and ·1662 grm. water.

This acid however still retained some impurities : on incineration it left 0·4 per cent. of ash (·5489 grm. giving ·0022 grm. ash), and examined for nitrogen it gave the following numbers :—

·4731 grm. burnt with soda-lime gave ·0150 grm. ammonio-chloride of platinum = 0·2 per cent. of nitrogen.

*h.* In order to separate these impurities the greater portion was dissolved in boiling absolute alcohol, and filtered from a slight residue ; the remainder, about an eighth, was converted into carminate of lead and digested with the boiling alcoholic solution for some hours ; the alcoholic tincture filtered off whilst hot and mixed with about six times its volume of anhydrous æther ; this threw down a bulky precipitate of a fine red colour, which was separated by filtration and the filtrate concentrated in a retort, and finally evaporated to dryness *in vacuo* (*h*).

*i.* The precipitate retained on the filter was dried *in vacuo*, then dissolved in as small a quantity of alcohol as possible, and again mixed with a large quantity of æther ; this determined a precipitate which was no longer of a fine red but of a brown colour, and on re-solution and similar treatment it diminished in quantity and became darker in colour, leaving the colouring matter in solution. From the filtrates a quantity of carminic acid (*i*) was obtained on evaporating to dryness *in vacuo*. It therefore appears that the æther precipitates a nitrogenous body which carries down with it variable quantities of carminic acid, according as a larger or smaller relative proportion is present. The carminic acid (*h*) was found to be free from phosphoric acid as well as nitrogen.

·3003 grm. burnt with soda-lime gave ·0015 grm. ammonio-chloride of platinum = 0·03 per cent. of nitrogen.

From this analysis I venture to assert that the colouring principle of cochineal contains no nitrogen, thus fully confirming the anticipation of Berzelius. We can now understand from the preparation of the specimen of carminic acid (*e*), that the method employed by Pelletier for the preparation of the substance he analysed was calculated to accumulate all the nitrogenous matter contained originally in his alcoholic decoction ; a fact which fully explains the large amount of nitrogen he obtained in his analysis.

An analysis of the carminic (*h*) acid by chromate of lead gave from—

VIII. ·3167 grm. ·6203 grm. carbonic acid and ·1402 water.

The following table exhibits the per-centge results deduced from the foregoing analyses: the specimens were all dried over sulphuric acid *in vacuo*, with the exception of analysis VII., in which the carminic acid was dried at 100° C.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	Mean.
Carbon ...	53·38	53·63	53·78	53·55	53·21	53·97	53·20	53·42	53·51
Hydrogen	5·20	5·14	5·12	5·19	5·04	5·39	4·59	4·92	5·07

By the analysis of a copper salt of carminic acid hereafter to be mentioned, it became probable that carminic acid might still retain, when only dried *in vacuo*, a portion of the solvents employed; a presumption which was supported by the analysis VII., in which the substance analysed had been dried at 100° C., and which gave a smaller per-centge of hydrogen. A portion of carminic acid (*i*), being first dried *in vacuo*, and then heated to a temperature of 121° C., was found to yield a small quantity of acetic acid, and was not altered in its properties, which were not in fact changed even at a temperature of 136° C.

In the following analyses the carminic acid, previously dried *in vacuo*\* and then at a temperature of 120° C., gave, on burning with chromate of lead, the following results:—

IX. ·3347 grm. (*h*) gave ·6648 grm. carbonic acid and ·1381 grm. water.

X. ·3583 grm. (*i*) gave ·7108 grm. carbonic acid and ·1504 grm. water.

These analyses give the following per-centge quantities:—

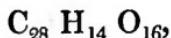
	IX.	X.
Carbon . . .	54·17	54·10
Hydrogen . .	4·58	4·66

The analysis IX. being of the same preparation as had served for analysis VIII., it is fair to presume that all the other specimens of carminic acid would have given the same per-centge quantities as the specimen (*h*) if dried at 120° C., as this particular specimen, dried *in vacuo*, yielded numbers in close accordance with the mean of the other analyses.

These numbers converted into the most simple expression lead to the following formula,  $C_{14} H_7 O_8$ ; but an analysis of a copper salt renders it probable that this formula has to be

\* The carminic acid fuses if exposed to a temperature of 120° C. without having been previously dried.

doubled, and that the composition of carminic acid is expressed by the formula,



as may be seen from the following table containing the comparison of the theoretical per-centages with the mean of analyses IX. and X.

	Theory.	Experiment.
C <sub>28</sub> . . 168	54·19	54·13
H <sub>14</sub> . . 14	4·52	4·62
O <sub>16</sub> . . <u>128</u>	<u>41·29</u>	<u>41·25</u>
	310	100·00

From the foregoing experiments, it seems that the best method of obtaining pure carminic acid is to precipitate the aqueous decoction by acetate of lead; to decompose the washed carminate of lead by hydrosulphuric acid, and to throw down the carminic acid once more by acetate of lead, previously mixed with acetic acid; to decompose the carminate of lead by hydrosulphuric acid; to evaporate to dryness and redissolve the carminic acid in absolute alcohol; then to digest the alcoholic tincture with carminate of lead; and lastly, to precipitate the trace of nitrogenous matter by æther, the pure carminic acid is obtained from the filtrate.

As thus prepared, carminic acid has the following properties. It is a purple brown friable mass, transparent when viewed by the microscope, and pulverizing to a fine red powder; soluble in water and alcohol in all proportions, very slightly soluble in æther, which does not however precipitate it from its alcoholic solution if free from nitrogenous matter. It is soluble without decomposition in concentrated hydrochloric and sulphuric acids. It is decomposed by chlorine, iodine and bromine, which change its colour to yellow, and the latter on warming or by standing gives a yellow precipitate soluble in alcohol. Nitric acid decomposes it even if highly diluted: I shall have occasion to refer to this decomposition presently. It bears a temperature of 136° C. without decomposition; on gradually increasing the temperature a quantity of an acid liquor is produced, and at a red heat it intumesces and gives off a small quantity of red fumes, which condense: it gives no trace of oily matter.

The aqueous solution has a feeble acid reaction; it does not absorb oxygen. A volume of this gas contained in a tube with carminic acid over mercury did not change by absorption after exposure for several months. The fixed alkalies and ammonia give no precipitate in the aqueous solution, merely changing its colour to purple; in the alcoholic tincture they

produce purple precipitates ; all the alkaline earths produce purple precipitates ; sulphate of alumina gives no precipitate, but on addition of a drop of ammonia the carminic acid is immediately taken down as a beautiful crimson lake ; acetates of lead, copper, zinc and silver give purple precipitates ; the latter is immediately decomposed, and silver deposited ; the nitrates of lead, mercury and silver reddish precipitates ; protocloride and bichloride of tin no precipitates, but change the colour to a deep crimson.

The acid character of carminic acid being so very little pronounced, I met with considerable difficulties in determining its atomic weight ; it is only with great reserve that I bring forward the formula before cited. Several attempts were made to produce soda, baryta, lead and copper compounds, but it was only with the copper salt that I obtained results agreeing in different preparations.

It seems that carminic acid attaches itself to salts, for it was found that the precipitants could be removed from the precipitates only with the greatest difficulty. I omit several soda, baryta and lead determinations which have not led to any satisfactory result, and confine myself to the statement of the result of the analysis of the copper compound. It was obtained by acidulating an aqueous solution of pure carminic acid with acetic acid, and then precipitating by the cautious addition of acetate of copper, so as to leave an excess of carminic acid in the liquid. The precipitate was well-washed by decantation (by which a great loss was sustained) and dried. It formed into masses of a bronze colour, very hard and difficult to powder. Two specimens were prepared at different times (*a* and *b*).

I. ·2800 grm. (*a*) dried at 100° C. left, after ignition and treatment with nitric acid and re-ignition, ·0330 grm. oxide of copper.

II. ·3782 grm. (*b*) dried at 100° C. gave ·0426 grm. oxide of copper.

III. ·4702 grm. (*b*) dried at 100° C. gave on burning with chromate of lead ·8210 grm. carbonic acid and ·1743 grm. water.

These numbers lead to the following per-centge results :—

	I.	II.	III.
Carbon . . .	...	...	47·62
Hydrogen . . .	...	...	4·12
Oxide of copper	11·78	11·27	

agreeing closely with the formula,  $C_{28}H_{14}O_{16}$ ,  $CuO$ , as will be seen from a comparison of the theoretical and experimental numbers.

		Calculated.	Found.
Carbon . . .	28	168	47·62
Hydrogen . . .	14	14	4·12
Oxygen . . .	16	128	36·74
Oxide of copper	1	39·6	11·52
		<hr/> 349·6	<hr/> 100·00
			100·00

*Action of Nitric Acid on Carminic Acid.*

*Nitrococcusic Acid.*—When acting with nitric acid on “carmine” (carminic acid), MM. Pelletier and Caventou obtained white acid crystals resembling oxalic acid, but differing from this acid in several of its properties. M. Arppe found that the acid produced was oxalic acid. In my experiments I obtained the following results:—One pound and a half of crude carminic acid was gradually introduced into ten pounds of nitric acid, spec. grav. 1·4, and digested at a moderate heat; a violent evolution of nitrous fumes succeeded each addition of the carminic acid; after the whole quantity had been introduced and the action had somewhat subsided, the mixture was transferred into a smaller vessel and the action continued at the boiling-point for about two hours; by this time the greater part of the nitric acid had evaporated, and on withdrawing the vessel from the fire and allowing the mixture to cool, a crystalline cake was obtained, which on examination was found to consist partly of a new acid and partly of oxalic acid. To separate the oxalic acid, it was dissolved in a large quantity of boiling water and treated with nitrate of lead as long as any precipitate formed; this was collected and decompensed by boiling with dilute sulphuric acid; the filtrate from the sulphate of lead yielded a large quantity of prismatic crystals of oxalic acid, which were obtained perfectly white and pure after two or three crystallizations with the aid of a little animal charcoal.

The yellow liquid filtered from the oxalate of lead was concentrated and separated from a fresh portion of oxalate which deposited on concentration, the evaporation was then continued until a large quantity of crystals formed; the solution on cooling deposited a very bulky mass of yellow rhombic prisms, which were drained and dried, and re-dissolved in a sufficient quantity of boiling water, which on cooling deposited the acid (for which I propose the name of nitrococcusic acid) in beautiful crystals free from any lead salt; it was recrystallized twice more, by which means it was obtained perfectly pure.

Several preparations were made, sometimes using pure car-

minic acid, at other times carminate of lead, with similar results.

The analyses of four different preparations dried at 100° C. gave, on burning with chromate of lead (unless otherwise stated), the following numbers :—

I. ·3152 grm. (*a*) gave ·3892 grm. carbonic acid and ·0561 grm. water.

II. ·2500 grm. (*a*) gave ·3080 grm. carbonic acid and ·0445 grm. water.

(For this analysis I am indebted to Mr. Nicholson.)

III. ·3068 grm. (*a*) gave ·3820 grm. carbonic acid and ·0502 grm. water.

IV. ·4498 grm. (*b*) gave ·5626 grm. carbonic acid and ·0757 grm. water.

V. ·4461 grm. (*c*) gave ·5515 grm. carbonic acid and ·0777 grm. water.

VI. ·4503 grm. (*d*) gave, on being burnt with oxide of copper, ·5585 grm. carbonic acid and ·0757 grm. water.

VII. ·4796 grm. (*c*) gave, on being burnt with oxide of copper, and a layer of copper twelve inches long used so as to completely decompose the binoxide of nitrogen, ·5882 grm. carbonic acid and ·0815 grm. water.

The foregoing analyses lead to the following per-centge quantities :—

	I.	II.	III.	IV.	V.	VI.	VII.
Carbon .	33·67	33·60	33·95	34·11	33·72	33·82	33·44
Hydrogen .	1·98	1·98	1·82	1·87	1·93	1·87	1·89

In the following experiments the nitrogen of the nitrococcusic acid was ascertained by burning with oxide of copper in an atmosphere of carbonic acid.

VIII. ·6808 grm. (*b*) dried at 100° C. gave 84 cub. cent. of moist nitrogen at 6°·5 C. and 0·7585 m., barometer corrected.

IX. ·7162 grm. (*c*) dried at 100° C. gave 91·5 cub. cent. of moist nitrogen at 17°·5 C. and 0·7641 m., barometer corrected.

These numbers correspond to the following per-centge quantities :—

	VIII.	IX.	Mean.
Nitrogen . .	15·03	14·92	14·97

X. In this experiment the nitrogen was determined according to Bunsen's\* method, which consists in burning the substance mixed with oxide of copper in the presence of copper turnings in a hard glass tube. The tube being freed from air by a stream of hydrogen, is then exhausted, sealed hermetically, and placed in an iron mould filled with plaster of Paris ; it is then heated to redness and allowed to cool. After the com-

\* Liebig's *Annalen*, vol. xxxvii. p. 27.

bustion, the gas is transferred into a graduated jar over mercury and its volume noted; the carbonic acid being absorbed by a potash ball, the volume is again read off. This analysis gave the following numbers:—

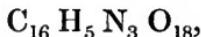
	Vol.	Temp.	Diff. of level.	Barom.
Carbonic acid + nitrogen (moist)	123	20°.7 C.	0m.0640	0m.7543
Nitrogen . . . . .	22.2	20°.0	0m.1650	0m.7529

The height of the column of mercury in the eudiometer above the level in the trough and the barometric column are corrected for temperature.

$$\begin{array}{l} \text{Carbonic acid + nitrogen corrected to } 0^\circ \text{ C. and barom. } 1^m = 76.84 \\ \text{Nitrogen} \quad \dots \quad \dots \quad 0^\circ \quad \dots \quad 1^m = 12.16 \\ \text{Carbonic acid} \quad \dots \quad \dots \quad 0^\circ \quad \dots \quad 1^m = 64.68 \end{array}$$

$\frac{64.68}{12.16} = 5.32$ , which is the ratio of carbon equivalents to one nitrogen equivalent.

The preceding analyses of nitrococcusic acid agree with the following formula, confirmed by the analyses of several of its compounds,



as will be seen on referring to the table.

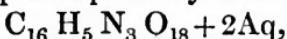
	Theory.		Experiment.
			Mean.
Carbon . . 16	96	33.45	33.75
Hydrogen . . 5	5	1.74	1.91
Nitrogen . . 3	42	14.63	14.97
Oxygen . . 18	144	50.18	49.37
	287	100.00	100.00

By analysis VII., in which the precaution was taken of using a very long layer of copper turnings, there was obtained, carbon 33.44, hydrogen 1.89; these numbers agree as closely as possible with the theoretical quantities, as does likewise the nitrogen determination (X.) by Bunsen's method; in this experiment the ratio of carbon equivalents to nitrogen equivalents was found to be as 5.32 to 1, or as 16 equivs. of carbon to 3.007 equivs. of nitrogen; taking analysis VII. as the basis of calculation, it gives 14.67 per cent. of nitrogen, the theoretical number being 14.63.

The acid, as it separates from its aqueous solution, contains water of crystallization, which it loses at 100° C.; four experiments gave the following results:—

•4800 grm. lost	•0289 grm.	= 6.02 per cent.
•6613 ... ...	•0395 ...	= 5.97 ...
•6586 ... ...	•0385 ...	= 5.84 ...
•4804 ... ...	•0289 ...	= 6.01 ...
Mean . . .		= 5.96 ...

This mean corresponds perfectly with the formula



as may be seen by a comparison of the theoretical and experimental numbers.

	Theory.	Experiment.
		Mean.
1 equiv. dry acid . . . .	287	94·10
2 ... water . . . .	18	5·90
1 ... crystallized nitrococcus acid . . . .	305	100·00
		100·00

*Properties of Nitrococcus Acid.*—It is of a yellow colour, crystallizing in rhombic plates, and presenting very different aspects, according to the circumstances under which it is crystallized. Its solution stains the skin yellow, it is soluble in cold, but considerably more so in hot water; soluble in alcohol, and very soluble in æther. All its salts dissolve readily in water, and most of them in alcohol; it deflagrates violently on being heated; it dissolves iron and zinc, becoming dark-coloured. It is decomposed by sulphuret of ammonium with separation of sulphur and the formation of the ammonia salt of a new acid, which I have not yet examined.

#### *Compounds of Nitrococcus Acid.*

*Nitrococcusate of Potash.*—I have prepared this salt by two different methods.

a. A solution of nitrococcus acid in boiling water was accurately saturated with carbonate of potash; by evaporation to a small bulk and cooling, the salt was obtained in small yellow crystals; it was purified by draining and recrystallizing.

b. An ætherial solution of the acid was precipitated by the cautious addition of an alcoholic solution of potash; the pale yellow precipitate washed with æther and dried, then dissolved in as small a quantity of cold water as possible, and the solution poured into about five times its bulk of absolute alcohol; after standing some time the salt crystallized in well-formed crystals; it was washed with æther and dried. The ætherial washings being added to the mother-liquor, a further portion was obtained and washed with æther. The latter process is less troublesome than the process a.

I. ·5469 grm. (a) dried at 100° C. were dissolved in a small quantity of boiling water and decomposed by sulphuric acid; dried in a water-bath, the nitrococcus acid, removed by æther and the residue ignited, gave ·2606 grm. sulphate of potash.

II. ·4383 grm. (b) dried at 132° C. gave ·2103 grm. sulphate of potash.

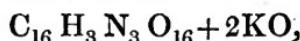
III. ·6251 grm. (b) dried at 100° C. and burnt with chro-

mate of lead, gave .6064 grm. carbonic acid and .0662 grm. water.

These numbers give the following per-centge quantities:—

	I.	II.	III.
Carbon . . .	...	...	26·46
Hydrogen . . .	...	...	1·18
Potash . . .	25·74	25·92	

corresponding with the formula



as may be seen by comparing the theoretical and experimental numbers.

	Theory.	Experiment.	Mean.
Carbon . 16	96	26·45	26·46
Hydrogen 3	3	.83	1·18
Nitrogen . 3	42	11·57	
Oxygen . 16	128	35·26	
Potash . 2	94	25·89	25·83
	363	100·00	

I was not successful in preparing a nitrococcusate of potash with one equivalent of fixed base; the method I adopted was saturating a given weight of acid with carbonate of potash, and then adding the same amount of acid to the bibasic potash salt; on washing with æther the greater part of the excess of acid was removed, leaving the bibasic salt behind.

*Nitrococcusate of Ammonia.*—This salt was prepared by passing an excess of dry ammoniacal gas through an ætherial solution of the acid dried in the atmosphere; the solution became turbid, and by standing for a short time deposited the salt in clusters of needles adhering firmly to the sides of the vessel; these were removed, washed with æther, and dried on bibulous paper. It is volatile, and sublimes on being heated, most probably with decomposition.

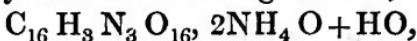
I. .6011 grm. of the salt dried *in vacuo* was dissolved in a small quantity of boiling water and decomposed by strong hydrochloric acid, which immediately separated the acid in crystals; the mixture was dried in a water-bath, and the nitrococcusic acid removed by æther, a little bichloride of platinum and alcohol being added to the aetherial washings to precipitate a trace of chloride of ammonium. The residue, precipitated as ammonio-chloride of platinum, gave .8208 grm. of the double chloride.

II. .6126 grm. dried *in vacuo* and burnt with oxide of copper, the mixture being made in the combustion-tube, gave :6525 grm. carbonic acid and .2191 grm. water.

These numbers correspond with the following per-centge quantities :—

	I.	II.
Carbon . . . . .	...	29·05
Hydrogen . . . . .	...	3·97
Oxide of ammonium . . .	15·91	

agreeing closely with the following formula,



as may be seen by a comparison of the theoretical and experimental numbers.

	Theory.	Experiment.
Carbon . 16	96	29·09
Hydrogen 12	12	3·64
Nitrogen . 5	70	21·21
Oxygen . 19	152	46·06
	330	100·00

Or

	Theory.	Experiment.
Acid . . . . . 1	269	
Water . . . . . 1	9	
Oxide of ammonium 2	52	15·76
	330	15·91

*Nitrococcusate of Baryta* was prepared by adding an excess of a solution of baryta to an aqueous solution of nitrococcusic acid, a stream of carbonic acid gas being passed through the solution to separate the excess of baryta. The solution was warmed, filtered and evaporated in a water-bath, and again filtered from a small quantity of carbonate of baryta. The evaporation being continued until a pellicle formed on the surface, the solution on cooling deposited this salt in minute yellow crystals. It is insoluble in alcohol, which precipitates it in the form of a jelly from the aqueous solution.

I. ·6750 grm. of substance dried at 100° C. and decomposed by sulphuric acid, gave ·3602 grm. of sulphate of baryta.

II. ·6439 grm. of nitrococcusate of baryta dried at 100° C. and burnt with chromate of lead, gave ·5185 grm. of carbonic acid and ·0800 grm. of water.

These numbers correspond to the following per-centge quantities :—

	I.	II.
Carbon . . . . .	...	21·96
Hydrogen . . . . .	...	1·38
Baryta . . . . .	35·06	

agreeing with the formula  $C_{16}H_3N_3O_{16} + 2BaO + 2HO$ , as may be seen from the following table:—

	Theory.	Experiment.
Carbon . 16	96·00	21·80
Hydrogen . 5	5·00	1·14
Nitrogen . 3	42·00	9·54
Oxygen . 18	144·00	32·71
Baryta . . 2	153·28	34·81
	440·28	100·00

*Nitrococcusate of Silver.*—I attempted to make this salt by boiling oxide of silver with an aqueous solution of nitrococcusic acid, but there was an evident decomposition of the acid, a large quantity of carbonic acid being evolved; after warming the filtered liquor a brown deposit was formed. On filtering off this brown deposit a silver salt was obtained by evaporation, which yielded on analysis—

Carbon . . . . .	23·64
Hydrogen . . . . .	1·26
Oxide of silver . . . . .	38·10

per-cent-age numbers not reconcilable with those of nitrococcusate of silver.

On decomposing a hot solution of this salt with hydrochloric acid a new acid was obtained, perfectly distinct from nitrococcusic acid; it crystallized in long needles; very insoluble in water, but soluble in æther and alcohol. I refrain from giving any further account of this acid until the study is completed.

In order to avoid decomposition the nitrococcusate of silver was prepared without the aid of heat, by dissolving carbonate of silver in a cold aqueous solution of nitrococcusic acid and evaporating the filtered solution *in vacuo* over sulphuric acid. The salt crystallized in long bulky needle-like crystals of a yellow colour; when dried at  $100^{\circ} C.$  the powdered salt becomes deep orange.

It is soluble in alcohol and water, and is highly explosive when heated; in small quantities it may be decomposed by a progressive heat without any violent action; but on attempting to decompose a quantity amounting to '45 grm. in a porcelain crucible, heated in an air-bath, the salt exploded with great violence, shattering the copper air-bath and driving fragments of the crucible through the copper; the temperature was noted just before the explosion, the thermometer standing at  $200^{\circ} C.$ ; the silver was therefore determined as chloride.

I. ·4698 grm. of substance (*a*) dried at 100° C. and decomposed by nitric acid and the silver precipitated by the addition of hydrochloric acid, gave ·2675 grm. chloride of silver.

II. ·5085 grm. of substance (*b*) dried at 100° C. gave ·2892 grm. chloride of silver.

III. ·8184 grm. of substance (*a*) dried at 100° C. and burnt with oxide of copper, gave ·5700 grm. carbonic acid and ·0554 grm. water.

Corresponding to the following per-centge quantities:—

	I.	II.	III.
Carbon . . . . .	...	...	18·99
Hydrogen . . . . .	...	...	0·75
Oxide of silver . . . .	46·03	45·97	

and agreeing closely with the following formula,



as may be seen by the following table:—

	Theory.		Experiment.
		Mean.	
Carbon . . . . 16	96	19·162	18·99
Hydrogen . . . 3	3	·599	·75
Nitrogen . . . 3	42	8·383	
Oxygen . . . 16	128	25·549	
Oxide of silver . 2	232	46·307	46·00
	501	100·000	

*Nitrococcusate of Copper.*—This was made by dissolving carbonate of copper in nitrococcusic acid and deposited on evaporation in pale apple-green needles. I made no analysis of this salt.

The following is a synoptical table of the analyses of nitrococcusic acid and its compounds:—

Hydrate of nitrococcusic acid .  $\text{C}_{16} \text{H}_3 \text{N}_3 \text{O}_{16} + 2\text{HO}$ .

Hydrate of nitrococcusic acid } as crystallized from water } ... ... + 2HO + 2Aq.

Nitrococcusate of potash . . . . . ... ... + 2KO.

Nitrococcusate of ammonia . . . . . ... ... + 2NH<sub>4</sub>O + Aq.

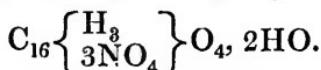
Nitrococcusate of baryta . . . . . ... ... + 2BaO + 2Aq.

Nitrococcusate of silver . . . . . ... ... + 2AgO.

The properties of nitrococcusic acid and its salts exhibit a great analogy with those of a number of acids obtained by the action of nitric acid on organic bodies, more especially nitropicric and styphnic acids, from which it differs by the greater solubility of its salts.

If we assume with many chemists the nitrogen of these

acids to exist in the form of hyponitric acid, the formula of nitrococcusic acid will be represented by



This acid would consequently derive from a non-nitrogenous acid, having the composition expressed by the formula



When I first began this investigation I imagined that a similar relation might exist between nitrococcusic acid and carminic acid; the analysis of these acids, however, as well as the simultaneous production of a large quantity of oxalic acid in its oxidation, showed that this view was erroneous, and that nitrococcusic acid was derived from carminic acid in a more complex manner. Some attempts were made to produce the non-nitrogenous acid, the coccusic acid, but unsuccessfully.

The experiments of MM. Cahours and Laurent on the oxidation of the oils of anise and of tarragon (*Oleum dracunculi*) have made us acquainted with anisic acid, the composition of which is  $\text{C}_{16} \text{H}_8 \text{O}_6$ . The formula agrees with the composition of the hypothetical hydrated coccusic acid.

Anisic acid, however, as well as nitranisic acid, being monobasic, it was not probable that the further introduction of the elements of hyponitric acid would convert it into a dibasic one; nevertheless it was my intention to have studied the further action of nitric acid on the acids mentioned, in order to obtain if possible trinitroanisic acid, and to compare this substance with the acid obtained from carminic acid, when an account of some new experiments of M. Cahours came under my notice, of the action of a mixture of concentrated sulphuric and nitric acids on anisic acid, by which he has succeeded in preparing trinitroanisic acid. The experiments of M. Cahours have not yet been published in detail, and from his short account it was not possible to decide on the identity or non-identity of nitrococcusic and trinitroanisic acids. A small specimen of anisic acid at my disposal was treated in the manner described by him; after acting for some time water threw down an acid, from the insolubility of which I conclude that these acids are only isomeric.

*Investigation of the Mother-liquor from which the Carminic Acid had been separated.*

On evaporating the mother-liquors of carminic acid and separating the lead held in solution by means of hydrosul-

phuric acid, they all gave the following results: on acquiring a syrupy consistence, a white chalky-like matter subsided; this was separated by filtration, and proved to be a new crystalline body. The liquor filtered off from this substance deposited a small quantity more on further concentration, and could only be dried to a soft tenacious mass, partly soluble in alcohol, the rest being soluble in water. From three pounds of cochineal five ounces of this soft matter were obtained, showing that the precipitation by a lead salt had effected the separation of carminic acid from a large quantity of foreign matters. This gelatinous matter appears to be of a complex character, but I have not yet examined it fully.

To purify the chalky-like matter, it was well-washed with cold water and crystallized twice by solution in boiling water and evaporation; it was then dissolved by boiling it in a just sufficient quantity of water; animal charcoal was now added, and the ebullition continued for a few minutes; the solution filtered whilst hot deposited on cooling a mass of silky crystalline tufts, completely filling the liquid, and when collected and dried they aggregated into paper-like masses of a silky aspect. I obtained in three experiments 4 parts of the new body from 1000 of cochineal.

I. ·4918 grm. of substance, preparation (*a*), dried *in vacuo* and burnt with oxide of copper, gave 1·0705 grm. carbonic acid and 0·2838 grm. water.

II. ·5680 grm. of substance (*b*) gave 1·2416 grm. carbonic acid and ·3160 grm. water.

III. ·4700 grm. of substance (*b*) gave 1·0210 grm. carbonic acid and ·2660 grm. water.

For the latter analysis I am indebted to the kindness of Mr. Nicholson.

A qualitative examination having pointed out the presence of nitrogen, it was determined by Varrentrapp and Will's method.

IV. ·5046 grm. of substance (*a*) dried *in vacuo* and burnt with soda-lime, gave ·6131 grm. ammonio-chloride of platinum.

V. ·5076 grm. of substance (*b*) gave ·6239 grm. ammonio-chloride of platinum.

From these numbers the following per-centages are calculated:—

	I.	II.	III.	IV.	V.
Carbon .	59·36	59·62	59·25		
Hydrogen .	6·41	6·18	6·29		
Nitrogen .	...	...	...	7·62	7·71

These per-centages, translated into the most simple expression, lead to the formula,  $C_{81} H_{11} NO_6$  as may be seen from the following table :—

	Theory.	Experiment.
		Mean.
Carbon . . . 18	108	59·668
Hydrogen . . 11	11	6·077
Nitrogen . . . 1	14	7·735
Oxygen . . . 6	48	26·520
	181	100·000

Careful and repeated examinations for sulphur proved the absence of this element as a component of the new white substance. I have been unable to produce a compound to control the proposed formula, though several methods were adopted; amongst others, I attempted to form a lead compound by adding acetate of lead to an ammoniacal solution of the substance; I obtained merely a bulky precipitate, consisting of little else than oxide of lead.

This substance is sparingly soluble in cold water, much more so in boiling water; insoluble in alcohol and æther; soluble in hydrochloric acid, which appears to be driven off by evaporation, leaving the substance in large crystals. In a large quantity of nitric acid it dissolves with a slight evolution of gas; the solution evaporated spontaneously furnishes long crystals, which are in all probability a new acid; if dissolved in a small quantity of nitric acid, the mixture becomes spontaneously heated, violent action takes place, and the product is lost; frequently the substance becomes blackened into charred masses. It is soluble in ammonia, from which it is again recovered by the evaporation of the ammonia. It is soluble in the fixed alkalies, and is precipitated from these solutions by saturating with an acid.

In a short paper, entitled "Valerianic Acid and a new body from Casein," Baron Liebig\* describes a new substance obtained by fusing casein with hydrate of potash until an evolution of hydrogen takes place along with ammonia. On saturating with acetic acid the aqueous solution of the fused mass an aggregate of fine needles was produced, which were purified by repeated solution in carbonate of potash and reprecipitation by acetic acid. A preliminary analysis led to the formula  $C_{16} H_9 NO_5$ , differing from the result I obtained in the analysis of the white substance from cochineal by two carbon, two hydrogen, and one oxygen. The properties of the two bodies being however so analogous, it is extremely probable that they are identical, a presumption I am sup-

\* Liebig's *Annalen*, vol. lvii. p. 127.

ported in by a comparison of a specimen kindly furnished me by Dr. Hofmann \*; further investigations will clear up this point: in the meantime I refrain from proposing a name, as Liebig † has lately proposed the name Tyrosine for the substance prepared from casein. As the latter body arises evidently from a process of oxidation, and as I had obtained the first crop of crystals from a liquid from which the colouring matter had been precipitated by the basic nitrate of lead, I thought that this body might owe its formation to the action of the nitric acid liberated by the sulphuretted hydrogen; but this supposition proved to be erroneous, for in later experiments in which acetate of lead had been used, the same body, and in exactly the same quantity, was obtained. From this we may assume that this substance is contained ready-formed in the cochineal insect.

My engagements for the present preventing me from continuing these researches, I must defer for a future period their completion, but hope to be enabled to communicate to the Society a second paper. In conclusion I may be allowed to express my thanks to my friend Dr. Hofmann for his valuable instruction in the methods of organic research, and his kind advice during the progress of this investigation.

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LXXIII. *On the Existence of Crystals with different primitive forms and physical properties in the Cavities of Minerals; with additional Observations on the New Fluids in which they occur.* By Sir DAVID BREWSTER, K.H., LL.D., F.R.S., and V.P.R.S. Edin.‡

[With a Plate.]

IN 1823 and 1826 I communicated to the Society two papers on the nature and properties of two immiscible fluids, which I discovered, in contact with each other, in the cavities of topaz and other minerals §. Although the facts contained in these papers were of so extraordinary a nature as to be received with scepticism by some, and with ridicule by others, yet I am not aware that, during the twenty years which have elapsed since their publication, any person has either repeated my observations, or advanced a single step in the same path of inquiry. In showing to strangers some of the leading phænomena of the two new fluids, my attention has been frequently recalled to the subject; but it was not till

\* This specimen had been prepared by Baron Liebig himself.—A.W.H.

† Researches on the Chemistry of Food, p. 16.

‡ Read before the Royal Society of Edinburgh on the 17th of February 1845, and published in their Transactions, vol. xvi. part 1. p. 11.

§ Edinburgh Transactions, vol. x. p. 1 and 407.

Phil. Mag. S. 3. No. 211. Suppl. Vol. 31.

last spring, when I discovered cavities in topaz filled with the most beautiful crystals of various form, that I was induced to undertake a new investigation of their nature and properties. In this investigation I have examined, with various magnifying powers, and both in common and polarized light, more than 900 specimens of topaz from Scotland, New Holland, and the Brazils; and I have had the good fortune to observe many new phænomena connected with mineralogy, chemistry, and physics, which, in addition to the interest which they may possess as scientific facts, promise to throw a strong light upon the existing theories of crystallization, and to bring before us some of those recondite operations which had been going on in the primitive rocks of our globe, before the commencement of vegetable or animal life.

### *1. On the Form and Position of the Strata in which the Cavities lie.*

The cavities which contain the two new fluids, and their accompanying crystals, sometimes occur single, and in groups more or less numerous; but, in general, they exist in millions, occupying extensive strata, which affect the transparency of the mineral, and render it unfit for the use of the jeweller, or even for the cabinet of the collector, who has not learned that it is in the deviations from her ordinary laws that Nature often discloses her deepest mysteries.

Although the strata of cavities sometimes occur, as in artificial salts, in planes parallel to the primary or secondary forms of the crystal, yet they occupy every *possible position* in reference to these planes; and we therefore cannot account for them by supposing that certain spaces have been left in the crystal, without the primitive molecules which ought to have been there deposited. The strata of cavities, too, have every possible curvature. From a plane surface they pass into a curved one, sometimes of variable curvature, and sometimes of contrary flexure, cutting and intersecting each other in the most capricious manner.

In the shape of the strata the same irregularity presents itself; their outline is sometimes rectilineal, sometimes curved, and sometimes singularly irregular. In some specimens the whole crystal is intersected with the strata; and it is extremely probable, though it is impossible to determine the fact, that in every specimen some edge or angle of the stratum touches the surface.

The succession of the cavities in composing the stratum, and their form in relation to the character of the stratum, present interesting phænomena. I have found specimens in

which the cavities lie in concentric arches, and have their sides concentric, and, as it were, a portion of the same arches, as if they had been formed under the influence of a rotatory force. In other cases they occupy parallel lines, and are sometimes so equidistant that they might be advantageously used as micrometers for microscopes. In one remarkable specimen they radiate from a centre, each radiation having a character of its own. One radiation will sometimes throw off a diverging branch, while two or more radiations will converge and then diverge again, subsequently uniting themselves into a single radiation.

When different strata of cavities lie parallel to each other in the specimen, which they sometimes do, to the number of four or five, each stratum has generally a distinct character; flat and exceedingly thin cavities occupying one stratum, very deep cavities occupying another, minute cavities which the highest magnifying powers can scarcely resolve occupying a third, while a fourth consists of the most irregular and indescribable forms.

When the forms of individual cavities are related to that of the stratum which contains them, they, of course, cut at all angles the primary and secondary planes of crystallization; and the same is true of insulated cavities of great length, which are sometimes turned, and twisted, and bent in the most capricious manner. It is impossible to read these details, and still more so to study the phænomena themselves, without being driven to the conclusion, that the strata of cavities must have been formed under the influence of forces propagated through a soft and plastic mass, and carrying along with them gases and vapours which came to a position of rest previous to the regular crystallization of the topaz. This conclusion, which I have been led to draw, in another paper, from a series of entirely different facts, will be still further confirmed by the phænomena of imbedded crystals, to which I shall have to refer in another section.

## 2. Additional Observations on the Nature and Properties of the two New Fluids.

In re-examining the phænomena exhibited by the two new fluids, I have found no occasion to modify or to correct any of the results contained in my former papers. In the cavities which appear to contain only one fluid, namely, the dense fluid, I have sometimes found a very small quantity of the volatile fluid, which, with a slight rise of temperature, passes into vapour, and prevents the apparent vacuity from disappearing by the application of a strong heat. When there is

no volatile fluid present in such cavities, the vacuity is a real one, and disappears entirely by the application of such a heat. If the heat is not instantly withdrawn on the disappearance of the vacuity, the crystal never fails to burst with great violence.

In some specimens of Brazil topaz I have found cavities with two fluids, and without any vacuity in the volatile fluid at the ordinary temperature of an apartment. In such cases I have generally produced a vacuity by the application of ice. Had heat been applied, the crystals would have burst, as there were no empty spaces into which the fluids could expand.

When the cavities are flat, and have their faces perpendicular to the axis of the crystal, or parallel to the planes of *easy cleavage*, the application of heat does not burst the crystal, but produces a very remarkable phænomenon. The cavity opens at its weakest point, and the fluid passes by starts, through a succession of resting places, to another part of the crystal where it finds the readiest exit. The fluid penetrates, as it were, the solid gem, and the laminæ which it has forced asunder in its passage, again close into optical if not into mechanical contact. If the heat is withdrawn when the first minute drop has passed, the laminæ unite, and we can discharge the rest of the fluid whenever we please till the cavity is exhausted. This phænomenon is represented in Plate III. fig. 1, where ABCD is a shallow cavity in a plate of topaz MN, and EF another cavity, which has been emptied of its fluid contents by reaching the surface at N, where it had been broken through. Upon looking at the cavity ABCD when slightly heated, I observed dark portions of fluid rushing from its sharp termination at D through the cavity at a, and then reappearing at b and c, and then passing into the empty cavity EF. The small lakes, as we may call them, at a, b and c, disappeared entirely when the discharged portions of fluid had passed, and reappeared with a change of form and size when the operation was repeated.

In a specimen of topaz possessed by Major Playfair, and seen by many individuals, a white ball passed from one cavity to the edge of the specimen, as if projected from a mortar; but by the application of too strong a heat it was shattered in pieces.

In my first paper of 1823\*, I have described and figured a phænomenon of an analogous kind; but as it appeared unexpectedly, and was instantly followed by the explosion of the crystal, I could neither observe it accurately, nor confirm what I did observe, by a repetition of the experiment. I have, therefore, some satisfaction in describing a similar phæno-

\* Edinburgh Transactions, vol. x. p. 11, plate 1. fig. 5, 6.

menon, seen frequently, and under more favourable circumstances, not only from its intrinsic interest, but because a distinguished philosopher had treated with an air of incredulity an observation which I had made of a similar kind. There can be no higher testimony to the novelty and importance of a scientific fact, than when a competent judge raises it to the supernatural.

I come now to describe a property of the dense fluid, so new and remarkable that it cannot fail to excite the attention of chemists. This fluid occupies the whole of a large cavity ABCDE, fig. 2, with the exception of a bubble at A, which must be either a vacuum, or a bubble of the expansible fluid, or the vapour of the dense fluid, or some gaseous body. It cannot be a vacuum, because it expands with heat, in place of being filled up by the expansion of the fluid. It cannot be the expansible fluid, because cold would contract it, and produce a vacuity. It cannot be the vapour of the expansible fluid, because there is no expansible fluid to throw it off, and it has not the optical properties of its vapour. It cannot be the vapour of the fluid in the cavity, for it does not disappear by the application of cold, and does not become a vacuity, which fills up by the expansion of the fluid. It is therefore an independent gas, which exhibits the following phænomena.

When heat is applied, the bubble A expands, not by the degradation of its circular margin passing into vapour, as in the vapour cavities described in a former paper, but by the rapid enlargement of its area. When it attains a certain size, it throws off a secondary bubble B, which passes over a sort of ridge or weir *mno*, in the bottom of the cavity, and settles at B. If the heat is continued, these two bubbles increase in size; but it was instantly withdrawn when B had begun to swell. As the topaz began to cool, both the bubbles A and B quickly contracted. The primary bubble A returned gradually to its original condition, and B, when reduced to a single speck, would have disappeared, had the cooling not been stopped. This speck swelled again by the application of heat, and so did the bubble A. When the speck at B was allowed to vanish, which it did on the spot which the bubble occupied, the fresh application of heat did not revive it at that spot, but merely expanded the primary bubble A, which again threw off a secondary bubble B, which exhibited by heat and cold the same phænomena as before. These experiments I repeated many times with the same result. It will naturally be asked, what was the condition of the fluid itself which has the property of expanding by heat; and what be-

came of it while a part of the space which it occupied was appropriated by the bubble B, and the addition to the bubble A? An accidental circumstance enables me to answer this question, which would have been otherwise a very perplexing one. Having applied too strong a heat to the specimen, the bubble A threw off beside B two or three smaller ones, which moved along the upper edge AE. My attention having been thus directed to this part of the specimen, I was surprised to observe a great number of capillary lines or pipes PQ, rising from the edge AE of the cavity, and into which the fluid was forcing itself, oscillating in these minute tubes like the mercury in a barometer, and sometimes splitting the laminæ between them. The force of cohesion, thus overcome by the expansive efforts of the fluid, predominated over the capillary attraction of the tubes and surfaces, and pressed back all the fluid into the cavity, when the body of fluid had contracted in cooling.

If we now consider the body which occupies the vacuity A as a gas, and, consequently, the other bubble B as the same, it follows that the whole of the gas in B was absorbed by the fluid while cooling, and again given out by an increase of temperature. The gas, when in the act of being discharged, took its course to the locality of the speck at B, and to the bubble A; but to the bubble A alone when the speck had disappeared.

Upon repeating these observations the cavity burst; and I have now before me its two halves, forming its upper and its under surface. The portion of the cavity at A has the same depth as the portion below *mno*, all the rest of the cavity being much shallower. There was a fine doubly refracting crystal at MN, which polarized the blue of the second order; and its outline is still left on the cavity. There was a sort of crystalline powder disseminated round MN to a considerable distance, and the roof of the bubble B, when the roof of the cavity was entire, was always mottled with this powder.

In a former paper, I have distinguished vapour cavities from common cavities, by the manner in which the vacuity in the expansible fluid disappears. In the one case, the vacuity gradually enlarges by the degradation, as it were, of its margin, as the fluid passes into vapour; in the other, the vacuity gradually diminishes till it disappears. I have since found cavities of an intermediate character, in which the vacuity, on the first application of heat, diminishes, and then, when it has contracted to a certain size, it begins to expand; and its margin becoming thinner and thinner, it finally passes into vapour.

### 3. On the Form and Position of Crystals in the Cavities of Topaz.

In a former paper I have described a moveable group of crystals of carbonate of lime, which I discovered in a cavity in quartz from Quebec, containing a fluid with the properties of water. The crystals to which I am about to call attention are of a very different kind, and possess a very different kind of interest.

The crystals which occupy the fluid cavities of topaz are either fixed or moveable. Some of the fixed crystals are often beautifully crystallized. They have their axes of double refraction coincident with those of the crystal, and, as I have ascertained by the examination of exploded cavities, they actually form part of the solid topaz, though they exist in the fluid cavity. One or two of these are shown in fig. 4, plate 19, of my paper of 1826\*, and they may be distinguished by their attachment to the sides of the cavity. In the same figure, as well as in figs. 10, 13, 20, and 21 of my paper of 1823†, I have drawn others which I then believed to be fixed, but which I have no doubt are moveable, and produced from one or other of the new fluids.

In re-examining my specimens of *topaz*, I have been surprised at the great number of cavities which contain crystals. In some there are only one; in very many there are two, three, and four; and in a great number of specimens the cavity is so crammed with them, like a purse full of money, that the circular vacuity has not room to take its natural shape, and often can scarcely be recognised, in its broken-down condition, among the jostling crystals.

The crystals of which I am treating are sometimes found in the volatile, and sometimes in the dense fluid, but chiefly in the latter. They are often found in an amorphous state in the narrow necks and narrow extremities of cavities, positions in which they remain fixed while they continue solid; and sometimes regularly formed crystals remain fixed between the prismatic edges of cavities, in consequence of having either fallen into that position, or of having been formed there.

The crystals in topaz cavities are, in general, beautifully crystallized, and have a great variety of forms. I have observed the following:—

1. The tetrahedron.
2. The cube.
3. The cube, truncated on its edges and angles.
4. The rhombohedron.

\* Edinburgh Transactions, vol. x.

† Ibid, plates 1 and 2.

5. The prism, with plain and pyramidal summits.
6. The flat octohedron, truncated on its edges and angles.
7. Rhomboidal plates.
8. Hexagonal plates.
9. Long rectangular plates.

Besides these, there are amorphous crystals and crystallized masses of various characters.

*4. On the Physical Properties of the Crystals in Topaz Cavities.*

Although it would be desirable to submit these crystals, as well as the fluids which contain them, to chemical analysis, yet the task is too difficult to be accomplished in the present state of chemical science. I must therefore limit my observations to such of the physical properties of these crystals as can be rendered visible to the eye.

When I first applied heat to the crystals under consideration, I employed a very fine specimen, with large and numerous crystallized cavities, of a prismatical form, containing both the new fluids. In this specimen there were seven cavities unlike all the rest, and each of them containing a single crystal, and apparently but one fluid, namely, the dense one. The cavities were exceedingly flat, and irregular in their shape, and very unlike one another. Upon applying the heat of only a lighted paper match beneath the plate of glass on which the specimen lay, I was surprised to see the crystals gradually lose their angles, and then slowly melt, till not a trace of them was visible. In this state one of the cavities had the appearance shown in fig. 3, where V was the vacuity, and v, v' other two bubbles, one of which v soon joined the principal one V. In all the other six cavities the crystals were speedily reproduced, always at the point where they disappeared, provided a small speck remained unmelted; but otherwise in different parts of the cavity. In the cavity AB, however, fig. 3, the crystal was very long in appearing. In the course of an hour, however, a fasciculus of minute crystals appeared in the centre of the vacuity, as in fig. 4, and to them the principal crystal attached itself, as in fig. 5, which exhibits a perfect rhomboidal plate, truncated on its obtuse angles. The elliptical vacuity was pressed into the shape of a heart; and, by the application of ice, I succeeded in precipitating the vapour of the expandible fluid, which existed in a very minute quantity in all the seven cavities. The expandible fluid is shown between the two heart-shaped outlines in the figure, and I repeatedly threw it into vapour, and reduced that vapour to a fluid state. The phænomenon now described, of the melting of the crystals, and their subsequent recrystallization, I have shown to various

persons; and it is very remarkable that they generally reappear in this specimen of the same form, though with considerable modifications.

Upon applying heat to other cavities containing several crystals, I obtained very different results. Some of them melted easily, others with greater difficulty; and some were not in the slightest degree affected by the most powerful heat I could apply. When the crystals melted easily, they were as quickly reproduced; sometimes reappearing more perfectly formed than before, but frequently running into amorphous and granular crystallizations.

In some specimens of topaz all the crystals in the cavities refuse to melt with heat, and seem not to suffer the slightest change in their form. Hence we are entitled to conclude, that the crystals possessing such different properties must be different substances; and this conclusion is amply confirmed by an examination of their optical properties.

In making this examination, I used a polarizing microscope, so constructed that the plane, passing through the optical axis of the topaz, could be readily placed either parallel or perpendicular to the plane of primitive polarization. In this case the field of the microscope is wholly obscure, in so far as the depolarizing action of the plate of topaz is concerned; but if there is any crystal in the topaz, either imbedded in its mass, or included in its cavities, that crystal will exhibit its doubly refracting structure, if it has any, by its depolarizing action. It may, indeed, happen,—and it does happen,—that the plane passing through their optical axes coincides, either accurately, or so nearly, with that of the topaz, that its depolarizing action is a minimum; but an experienced observer will have no difficulty in distinguishing this want of depolarization by position, from the want of it by structure.

When the specimen of topaz is rich in cavities full of crystals, the display of luminous and coloured crystalline forms in the dark field of the microscope, indicating, too, the imprisonment of fluids, and the condensation of gases before vegetable or animal life had visited our primæval globe, was as interesting to the imagination and the judgement as it was beautiful to the eye. Having had the privilege of being the first to see it, I felt the full influence of the sight; and I have again and again contemplated it with renewed wonder and delight. When the cavities are so numerous as to mock calculation, and so infinitely small as to yield no visible outline to the highest powers, the bright twinkle of a crystalline atom within them reveals to us their nature as well as their contents.

In the examination of the individual crystals, many interest-

ing facts present themselves to our notice. The crystals of the tessular class, which are modifications of the cube, are very numerous, and have no action upon polarized light. Many of them melt easily, while others refuse to yield to the action of heat; and hence there must be two different substances in the cavities which assume the same shape. In like manner, some of the doubly refracting crystals melt readily, others with very great difficulty, and others not at all; so that there must be *three* different substances, which belong to the classes of forms that give double refraction; a conclusion which is confirmed by the different secondary forms which I have already enumerated.

I have seldom found any crystals in these cavities which depolarize white light, or the highest order of colours. I have found some that depolarize *four* orders of colours; and when the crystal which does this is a flat hexagonal plate, it is highly interesting to see it pass through all the tints which these orders include, while slowly melting, and again reproducing them during its recrystallization.

In a cavity which was so placed as to be entirely black from the total reflexion of the light which fell upon it, I observed three *white* openings, *a*, *b*, *c*, of a crystalline form (see fig. 6). These appeared to be fixed crystals, or rather parts of the topaz, surrounded by a cavity. I found, however, that the hexagonal one *C* depolarized white light, while the rest had no action upon polarized light. Upon applying heat, the crystal *c* melted, and took up a position at *c*, fig. 15, in a narrower part of the cavity, where it remains of an irregular form, having been repeatedly melted and recrystallized. Upon turning the cavity into a position where it became transparent, I found that there was no fluid whatever in the cavity; so that we have here an example of a crystal melting and recrystallizing without having been dissolved in one of the fluids. From the irregular state of the laminæ close to this cavity, there is every appearance of the fluids having escaped from one of its extremities.

In the course of these observations, I observed a phænomenon, produced by heat, of the most novel and surprising kind, and one which I feel myself utterly unable to explain. It presented itself when I was studying the very interesting collection of crystals in the cavity *AB*, fig. 8. This cavity is filled with the dense fluid, in which there is a vacuity *V*: the fluid swells to such a degree with heat as to diminish very perceptibly the size of this vacuity; and as I can find no trace of any portion of the volatile fluid, I have no doubt that this vacuity would disappear by an increased degree of heat. The

fear, however, of bursting so rare and interesting a cavity, has prevented me from making this experiment. The cavity contains a great number of crystals of different forms, not one of which melts with heat, and almost all of which possess double refraction. When I first submitted this cavity to the microscope, there were *five* small crystals lying between D and the vacuity V; one a flat prism, another a hexagonal plate, a third amorphous, and a fourth and fifth two irregular halves of a hexagon. Upon the first application of heat, one or two of these crystals leapt from their resting place, and darted to the opposite side of the cavity. In a few seconds the others quitted their places one after another, performing the most rapid and extraordinary rotations. One crystal joined another, and, at last, four of them thus united revolved with such rapidity as completely to efface their respective shapes. They then separated on the withdrawal of the heat, and took the position which their gravity assigned them. On another occasion, a long flat prism performed the same rotation round its middle point; and I have repeated the experiment so often, in showing it to others, that the small crystals have been driven between the inclined edges of the cavity, from which I cannot extricate them. I have succeeded, however, in conducting a fine octohedral crystal, truncated on its edges and angles, into the arena at D, where I have just seen it perform its rotation, as indicated by the concentric circles on the right-hand of D.

In seeking for the cause of so extraordinary a phænomenon, we are reminded of the rotations of camphor and other volatile substances; but in this case no gas or matter of any kind could be thrown off without becoming visible in the fluid. The pyro-electricity of topaz next suggests itself as a moving power; but though it might produce attractions and repulsions, we cannot see how it could turn a crystal upon its axis. The experiments of Libri and Fresnel, on the repulsions which heated bodies exert upon each other at sensible distances, afford us as little aid. They may enable us to account for the mere displacement of the crystals by the application of heat, or for their sudden start from their places of rest, but they do not supply us with a force fitted to give and to sustain a rapid rotatory movement.

I have already had occasion to state, that the cavities often burst when too much heat is applied to the specimen. This generally takes place by a separation of the laminæ, which fly off in splinters; but when the burst cavity is large and insulated, a piece of the solid crystal is scooped out on its weakest side. Sometimes a great number of cavities explode at the same time, and when they are small, or exist in a part

of the crystal where there are no large ones, the explosive force is not strong enough to separate the laminæ. The fluid is merely driven between the laminæ to a small distance around the cavity, and shows itself as a dark brown powdery matter, encircling the cavity as the burr of a comet does its nucleus. When the cohesion of the laminæ is great, it resists the explosive force over a large cavity, and the contents of the cavity are thrown to a considerable distance around it, and remains between the laminæ, either as a sort of powder, or as a congeries of minute crystals, which are sometimes large enough to show their depolarizing action. When the laminæ separate, we find this crystalline matter either fluid or indurated; exhibiting, when fluid, the extraordinary properties described in my former papers. If we breathe upon the indurated matter it becomes fluid, recrystallizes in new spiculæ and crystals; and, on several occasions, I have found fine examples of circular crystallization.

After the explosion of cavities containing only the dense fluid, I have been surprised to find, and that in large cavities, that no trace of matter was left upon the sides of the cavity or around it. Whether this arose, as the fact seems to indicate, from the dense fluid being a condensed gas, or from some other cause, it will require new experiments to determine.

In a very remarkable specimen, in which the cleavage plane passed through a great number of large flat cavities, the brown matter has been lodged near to the edges of each cavity, and marks them out even to the unassisted eye. These cavities were filled almost solely with the volatile fluid; and since the faces of the cavities are corroded as if by the action of a solvent, developing crystalline forms, there is reason to think that the fluid has exercised this action, and that the phænomenon is analogous to that external action, on the faces of hundreds of Brazil topazes in my possession, which I have described in the Cambridge Transactions\*, and the singular optical figure formed by which, I have represented in a late volume of the Transactions of this Society†.

The only chemical experiment on the contents of these cavities, which I have had occasion recently to make, is perhaps worth reporting. One angle of a cavity was blown off by its explosion, and though the fluids escaped, a pretty large prismatic crystal remained within the cavity. I introduced water and alcohol successively into the cavity, and raised them to a considerable heat; but they had no effect in dissolving the crystal.

\* Vol. ii. plate 1. fig. 15.

† Edinburgh Transactions, vol. xiv. plate 10. figs. 1, 2.

### 5. *On Solid Crystals and Crystalline Masses imbedded in Topaz.*

Among the new phænomena which this section embraces, there is at least one intimately connected with the subject of the fluid cavities. How far the other phænomena may have any such connexion, it remains to be seen.

The imbedded crystals to which I refer, presented themselves to me while the specimens which contain them were exposed to polarized light. Mineralogists have been long familiar with the beautiful crystals of titanium, imbedded in quartz, and I have found the same mineral imbedded under still more interesting circumstances in the Brazilian amethysts.

In topaz, however, the imbedded crystals have never been noticed, and I have fortunately obtained specimens, in which they are displayed with singular beauty. Their axes of double refraction are not coincident with those of the topaz; and hence they are seen in the obscure field of the microscope splendid with all the colours of polarized light. These crystals are equally transparent with the topaz, with a few slight exceptions. They sometimes polarize five or six orders of colours; and, in general, they have very beautiful crystalline forms, which can be seen by the microscope in common light. In some cases they are mere crystalline masses, often of a reniform shape, but still with regular axes of double refraction.

In some specimens of Brazil topaz, the crystals occur in branches or groups of singular beauty, consisting of prisms and hexagonal plates, connected apparently by filaments of some opaque matter.

I have occasionally met with another interesting variety of them, which *have no visible outline* by common light, and which could never have been detected but by the polarizing microscope. In one of these cases, the crystalline mass, which is nearly spherical, lies in a crowded group of small fluid cavities, none of which enters its mass; a complete proof that the cavities were formed in the soft mass of topaz, when it encircled the indurated crystal.

Along with these interesting phænomena, another occasionally occurs, which may still require a further examination. I have observed *apparent* doubly refracting crystals, which differ in some essential points from those which have been described. They depolarize a uniform, or nearly a uniform tint, notwithstanding the different thicknesses through which the polarized light passes; and that tint is less brilliant than in the real imbedded crystals. I conceive, therefore, that they are crystallized cavities, having their inner surfaces coated with a doubly

refracting crust. This is, in itself, a very natural supposition, seeing that the fluid may have discharged its gaseous portion, and left behind it the matters which it held in solution. The cavities however, of this kind, which I have described in a former paper, have no depolarizing action; and I find that those now under consideration have regular axes of double refraction. Hence the matter which covers them must be a regular crystalline shell, with optical and crystallographic axes—a phænomenon which has no parallel in mineralogy.

St. Leonard's College, St. Andrew's,  
February 15, 1845.

#### LXXIV. *Observations on Chloric Acid and the Chlorates.* By LEWIS THOMPSON.

*To the Editors of the Philosophical Magazine and Journal.*

GENTLEMEN,

A N easy and œconomical mode of preparing chloric acid and some of the chlorates has not been described in any chemical work that I am aware of: the following will be found to answer extremely well.

Dissolve in two separate portions of boiling water one atom (122·81) of chlorate of potash, and one atom (168·34) of bitartrate of ammonia; mix the two solutions together, and set the whole aside in order that the bitartrate of potash may crystallize; then mix the clear solution with an equal bulk of alcohol, and filter or pour off the alcoholic solution of chlorate of ammonia, which must now be boiled in a flask or other narrow-necked vessel, with an excess of recently-precipitated carbonate of baryta, until the ammonia is expelled, water being occasionally added; then filter the fluid, evaporate, and crystallize. In dissolving the chlorate of potash and bitartrate of ammonia, as little water must be used as possible.

The chlorates of strontia and lime may be prepared in a similar manner; and the metallic chlorates are easily prepared by decomposing the chlorate of baryta by means of a sulphate of the base required.

Chloric acid is best obtained by dissolving a given weight of chlorate of baryta, and adding no more sulphuric acid than is sufficient to combine with the base; several hours or even days, however, appear necessary to effect this decomposition in the cold; after which the whole may be filtered and carefully evaporated at a low heat. When sulphuric acid is added to a solution of the chlorate of baryta, as long as it gives a precipitate, I have always found an excess of it in the chloric acid.

The bitartrate of ammonia may be readily made by dissolving tartaric acid in water, saturating one-half of the solution with ammonia or its carbonate, and adding to this the remaining half of the liquid tartaric acid; the bitartrate of ammonia immediately precipitates.

For pyrotechnical purposes, the chlorates of baryta, strontia, lead, &c. may be made without alcohol. With combustibles containing hydrogen, the chlorate of baryta produces a green flame of surpassing brilliancy; and the chlorate of strontia, although somewhat deliquescent, is much superior as a crimson to the nitrate of that earth.

I am, Gentlemen,

Your most obedient Servant,

Byker Bar, Newcastle-on-Tyne,  
October 14, 1847.

LEWIS THOMPSON.

**LXXV. On Quaternions; or on a New System of Imaginaries in Algebra.** By Sir WILLIAM ROWAN HAMILTON, LL.D., V.P.R.I.A., F.R.A.S., Corresponding Member of the Institute of France, &c., Andrews' Professor of Astronomy in the University of Dublin, and Royal Astronomer of Ireland.

[Continued from p. 293.]

51. IT has been shown\* that if the two symbols  $\iota$ ,  $\kappa$  denote certain constant vectors, perpendicular to the two cyclic planes of an ellipsoid, and if  $v$ ,  $\tau$  denote two other and variable vectors, of which the former is normal to the ellipsoid at any proposed point upon its surface, while the latter is tangential to a line of curvature at that point, then the directions of these four vectors  $\iota$ ,  $\kappa$ ,  $v$ ,  $\tau$  are so related to each other as to satisfy the condition †

$$S.v\tau\iota\kappa=0 \text{ (49.), article 47;}$$

S being the characteristic of the operation of taking the scalar part of a quaternion. And because the two latter of these four directions, namely the directions of the normal and tangential vectors  $v$  and  $\tau$ , are always perpendicular to each other, this additional equation has been seen to hold good:

$$S.v\tau=0 \text{ (36.), article 45.}$$

Retaining the same significations of the symbols, and carrying forward for convenience the recent numbering of the formulæ,

\* See the Philosophical Magazine for October 1847; or Proceedings of the Royal Irish Academy for July 1846.

† Inadvertently transcribed as  $S.v\tau\iota\kappa=0$ , towards the end of the last communication to this Magazine: but correctly printed in the formula (49.) here referred to.

it is now proposed to point out some of the modes of combining, transforming, and interpreting the system of these two equations, consistently with the principles and rules of the Calculus of Quaternions, from which the equations themselves have been derived.

52. Whatever two vectors may be denoted by  $\iota$  and  $\tau$ , the ternary product  $\tau\iota\tau$  is always a *vector form*, because (by article 20) its scalar part is zero; and on the other hand the square  $\tau^2$  is a pure scalar: therefore we may always write

$$\tau\iota\tau = \mu\tau^2, \quad \tau\iota = \mu\tau, \quad \dots \quad \dots \quad \dots \quad (52.)$$

where  $\mu$  is a new vector, expressible in terms of  $\iota$  and  $\tau$  as follows:

$$\mu = \tau\iota\tau^{-1}; \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (53.)$$

so that it is, in general, by the principles of articles 40, 41, 42, 43, the *reflexion* of the vector  $\iota$  with respect to the vector  $\tau$ , and that thus the direction of  $\tau$  is exactly intermediate between the directions of  $\iota$  and  $\mu$ . In the present question, this new vector  $\mu$ , defined by the equation (53.), may therefore represent the reflexion of the first cyclic normal  $\iota$ , with respect to any reflecting line which is parallel to the vector  $\tau$ , which latter vector is tangential to one of the curves of curvature on the ellipsoid. Substituting for  $\tau\iota\tau$  its value (52.), in the lately cited equation (49.), and suppressing the scalar factor  $\tau^2$ , we find this new equation :

$$S.\nu\mu\xi = 0; \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (54.)$$

which, in virtue of the general *equation of coplanarity* assigned in the 21st article (Phil. Mag. for July 1846), expresses that the reflected vector  $\mu$ , the normal vector  $\nu$ , and the second cyclic normal  $\xi$ , are parallel to one common plane. This result gives already a characteristical geometric property of the lines of curvature on an ellipsoid, from which the directions of those curved lines, or of their tangents ( $\tau$ ), can generally be assigned, at any given point upon the surface, when the direction of the normal ( $\nu$ ) at that point, and those of the two cyclic normals ( $\iota$  and  $\xi$ ), are known. For it shows that if a straight line  $\mu$  be found, in any plane parallel to the given lines  $\nu$  and  $\xi$ , such that the bisector  $\tau$  of the angle between this line  $\mu$  and a line parallel to the other given line  $\iota$  shall be perpendicular to the given line  $\nu$ , then this bisecting line  $\tau$  will have the sought direction of a tangent to a line of curvature. But it is possible to deduce a geometrical determination, or construction, more simple and direct than this, by carrying the calculation a little further.

53. The equation (52.) gives

$$(\mu + \nu) \tau = \tau \mu + \nu \tau = V^{-1} 0, \dots \quad (55.)$$

this last symbol  $V^{-1} 0$  denoting generally any quaternion of which the vector part vanishes; that is any pure scalar, or in other words any real number, whether positive or negative or null. Hence  $\mu + \nu$  and  $\tau$  denote, in the present question, two coincident or parallel vectors, of which the directions are either exactly similar or else exactly opposite to each other; since if they were inclined at any actual angle, whether acute or right or obtuse, their product would be a quaternion, of which the vector part would not be equal to zero. Accordingly the expression (53.) gives this equation between tensors,

$$T\mu = T\nu; \dots \quad (56.)$$

so that the symbols  $\mu$  and  $\nu$  denote here two equally long straight lines; and therefore one diagonal of the equilateral parallelogram (or rhombus) which is constructed with those lines for two adjacent sides bisects the angle between them. But by the last article, this bisector has the direction of  $\tau$  (or of  $-\tau$ ); and by one of those fundamental principles of the geometrical interpretation of symbols, which are *common* to the calculus of quaternions and to several earlier and some later systems, the symbol  $\mu + \nu$  denotes generally the intermediate diagonal of a parallelogram constructed with the lines denoted by  $\mu$  and  $\nu$  for two adjacent sides: we might therefore in this way also have seen that the vector  $\mu + \nu$  has, in the present question, the direction of  $\pm \tau$ . This vector  $\mu + \nu$  is therefore perpendicular to  $\tau$ , and we have the equation

$$0 = S.v(\mu + \nu), \text{ or } S.v\mu = -S.v\nu. \dots \quad (57.)$$

But by (56.), and by the general rule for the tensor of a product (see art. 20), we have also

$$T.v\mu = T.v\nu; \dots \quad (58.)$$

and in general (by art. 19), the square of the tensor of a quaternion is equal to the square of the scalar part, minus the square of the vector part of that quaternion; or in symbols (Phil. Mag., July 1846),

$$(TQ)^2 = (SQ)^2 - (VQ)^2.$$

Hence the two quaternions  $v\mu$  and  $v\nu$ , since they have equal tensors and opposite scalar parts, must have the squares of their vector parts equal, and those vector parts themselves must have their tensors equal to each other; that is, we may write

$$(V.v\mu)^2 = (V.v\nu)^2, \quad TV.v\mu = TV.v\nu: \dots \quad (59.)$$

and may regard these two vector parts of these two quaternions, or of the products  $v\mu$  and  $v_i$ , as denoting two equally long straight lines. Consequently the vector  $\pm v\tau$ , which has the direction of the line represented by the pure vector product  $v(\mu + i)$ , or by the sum  $V.v\mu + V.v_i$  of two equally long vectors, has at the same time the direction of the sum of the two corresponding *versors* of those vectors, or that of the sum of their *vector-units*; so that we may write the equation

$$t v \tau = U V. v \mu + U V. v_i, \dots \quad (60.)$$

where  $U$  is (as in art. 19) the characteristic of the operation of taking the versor of a quaternion, or of a vector; and  $t$  is a scalar coefficient. Again, the equation  $0 = S. v \mu x$ , (54.), which expresses that the three vectors  $v, \mu, x$  are coplanar, shows also that the two vectors  $V.v\mu$  and  $V.vx$  are parallel to each other, as being both perpendicular to that common plane to which  $v, \mu$ , and  $x$  are parallel; hence we have the following equation between two versors of vectors, or between two vector-units,

$$U V. v \mu = \pm U V. v x; \dots \quad (61.)$$

and therefore instead of the formula (60.) we may write

$$t \tau = v^{-1} U V. v_i \pm v^{-1} U V. v x. \dots \quad (62.)$$

In this expression for a vector touching a line of curvature, or parallel to such a tangent, the two terms connected by the sign  $\pm$  are easily seen to denote (on the principles of the present calculus) two equally long vectors, in the directions respectively of the projections of the two cyclic normals  $i$  and  $x$  on a plane perpendicular to  $v$ ; that is, on the tangent plane to the ellipsoid at the proposed point, or on any plane parallel thereto. If then we draw two straight lines through the point of contact, bisecting the acute and obtuse angles which will in general be formed at that point by the projections on the tangent plane of two indefinite lines drawn through the same point in the directions of the two cyclic normals, or in directions perpendicular to the two planes of circular section of the surface, *the two rectangular bisectors of angles, so obtained, will be the tangents to the two lines of curvature*: which very simple construction agrees perfectly with known geometrical results, as will be more clearly seen, when it is slightly transformed as follows.

54. If we multiply either of the two tangential vectors  $\tau$  by the normal vector  $v$ , the product of these two rectangular vectors will be, by one of the fundamental and *peculiar*\* principles,

\* See the author's Letter of October 17, 1843, to John T. Graves, Esq., printed in the Supplementary Number of the Philosophical Magazine for December 1844: in which Letter, the three fundamental symbols  $i, j, k$  were what it has been since proposed to name *direction-units*.

ples of the calculus of quaternions, a third vector rectangular to both; we shall therefore only pass by this multiplication, so far as *directions* are concerned, from one to the other of the tangents of the two lines of curvature: consequently we may omit the factor  $v^{-1}$  in the second member of (62.), at least if we change (for greater facility of comparison of the results among themselves) the ambiguous sign  $\pm$  to its opposite. We may also suppress the scalar coefficient  $t$ , if we only wish to form an expression for a line  $\tau$  which shall have the required *direction* of a tangent, without obliging the *length* of this line  $\tau$  to take any previously chosen value. The formula for the system of the two tangents to the two lines of curvature thus takes the simplified form :

$$\tau = UV.vi \mp UV.vk; \dots \dots \quad (63.)$$

in which the two terms connected by the sign  $\mp$  are two vector-units, in the respective directions of the traces of the two cyclic planes upon the tangent plane. The tangents to the two lines of curvature at any point of the surface of an ellipsoid (and the same result holds good also for other surfaces of the second order), are therefore parallel to the two rectangular straight lines which bisect the angles between those traces; or they are themselves the bisectors of the angles made at the point of contact by the traces of planes parallel to the two cyclic planes. The discovery of this remarkable geometrical theorem appears to be due to M. Chasles. It is only brought forward here for the sake of the *process* by which it has been above deduced (and by which the writer was in fact led to perceive the theorem before he was aware that it was already known), through an application of the method of quaternions, and as a corollary from the geometrical construction of the ellipsoid itself to which that method conducted him\*. For that new geometrical *construction* has been shown (in a recent Number of this Magazine) to admit of being easily *retranslated* into that quaternion form of the *equation* † of the ellipsoid, namely

$$T(i\rho + j\sigma + k\tau) = x^2 - t^2, \text{ equation (9.), art. (38.),}$$

as an *interpretation* of which equation it had been assigned by the present writer; and then a *general* method for investigating by quaternions the directions of the lines of curvature on *any curved surface whatever*, conducts, as has been shown (in

\* See the Numbers of the Philosophical Magazine for June, September, and October 1847; or the Proceedings of the Royal Irish Academy for July 1846.

† Another very simple construction, derived from the same quaternion equation, and serving to generate, by a moving sphere, a system of *two reciprocal ellipsoids*, will be given in an early Number of this Magazine.

articles 46 and 47), to the equation of those lines for the ellipsoid,

$$S \cdot v\tau i\tau x = 0 \quad (49.)$$

from which, when combined with the general equation  $S \cdot v\tau = 0$ , the formula (63.) has been deduced, and geometrically interpreted as above.

55. Another mode of investigating generally the directions of those tangential vectors  $\tau$  which satisfy the system of the two conditions in art. 51, may be derived from observing that those conditions fail to distinguish one such tangential vector from another in each of the two cases where the variable normal  $v$  coincides in direction with either of the two fixed cyclic normals,  $i$  and  $x$ ; that is, at the four *umbilical points* of the ellipsoid, as might have been expected from the known properties of that surface. In fact if we suppose

$$v = mi, \quad S \cdot i\tau = 0, \quad \dots \quad (64.)$$

where  $m$  is a scalar coefficient, that is if we attend to either of those two opposite *umbilics* at which  $v$  has the direction of  $i$ , we find the value

$$v\tau i\tau x = m(i\tau)^2 x, \quad \dots \quad (65.)$$

which is here a vector-form, because by (64.) the product  $i\tau$  denotes in this case a *pure vector*, so that *its square (like that of every other vector in this theory) will be a negative scalar*, by one of the fundamental and *peculiar\** principles of the present calculus; the scalar part of the product  $v\tau i\tau x$  therefore vanishes, or the condition (49.) is satisfied by the suppositions (64.). Again, if we suppose

$$v = m'x, \quad \dots \quad (66.)$$

$m'$  being another scalar coefficient, that is if we consider either of those two other opposite umbilics at which  $v$  has the direction of  $x$ , we are conducted to this other expression,

$$v\tau i\tau x = m'x\tau i\tau x; \quad \dots \quad (67.)$$

which also is a vector-form, by the principles of the 20th article. In this manner we may be led to see that if in general we decompose, by orthogonal projections, each of the two cyclic normals,  $i$  and  $x$ , into two partial or component vectors,  $i'$ ,  $i''$ , and  $x'$ ,  $x''$ , of which  $i'$  and  $x'$  shall be tangential to the surface, or perpendicular to the variable normal  $v$ , but  $i''$  and  $x''$  parallel to that normal, in such a manner as to satisfy the two sets of equations,

$$\begin{aligned} i &= i' + i''; \quad S \cdot i'v = 0; \quad V \cdot i''v = 0; \\ x &= x' + x''; \quad S \cdot x'v = 0; \quad V \cdot x''v = 0; \end{aligned} \quad \left. \right\} \quad \dots \quad (68.)$$

\* See the author's letter of October 17, 1843, already cited in a note to article 54.

then, on substituting these values for  $i$  and  $x$  in the condition (49.), or in the equation  $0 = S \cdot v \tau i \tau x$ , the terms involving  $i''$  and  $x''$  will vanish of themselves, and the equation to be satisfied will become

$$0 = S \cdot v \tau i' \tau x'; \quad \dots \quad (69.)$$

which is thus far a simplified form of the equation (49.), that three of the four directions to be compared (namely those of  $i'$ ,  $x'$ , and  $\tau$ ) are now parallel to one common plane, namely to the plane which touches the ellipsoid at the proposed point, and to which the fourth direction (that of  $v$ ) is perpendicular. Decomposing the two quaternion products,  $\tau i'$  and  $\tau x'$ , into their respective scalar and vector parts, by the general formulæ,

$$\begin{aligned} \tau i' &= S \cdot \tau i' + V \cdot \tau i'; \\ \tau x' &= S \cdot \tau x' + V \cdot \tau x'; \end{aligned} \quad \dots \quad (70.)$$

and observing that the vectors  $V \cdot \tau i'$  and  $V \cdot \tau x'$  both represent lines parallel to  $v$ , because  $v$  is perpendicular to the common plane of  $\tau, i', x'$ ; so that the three following binary products,  $V \cdot \tau i' \cdot V \cdot \tau x', vV \cdot \tau i', vV \cdot \tau x'$ , are in the present question scalars; we find that we may write

$$S \cdot v \tau i' \tau x' = v S \cdot \tau i' \cdot V \cdot \tau x' + v V \cdot \tau i' \cdot S \cdot \tau x'. \quad \dots \quad (71.)$$

Hence the equation (69.) or (49.) reduces itself, after being multiplied by  $v^{-1}$ , to the form

$$S \cdot \tau i' \cdot V \cdot \tau x' + V \cdot \tau i' \cdot S \cdot \tau x' = 0; \quad \dots \quad (72.)$$

which gives, in general, by the rules of the present calculus,

$$\frac{V \cdot i' \tau}{S \cdot i' \tau} = \frac{V \cdot \tau x'}{S \cdot \tau x'}; \quad \dots \quad (73.)$$

and by another transformation,

$$\frac{V \cdot i' \tau^{-1}}{S \cdot i' \tau^{-1}} = - \frac{V \cdot x' \tau^{-1}}{S \cdot x' \tau^{-1}}; \quad \dots \quad (74.)$$

which may perhaps be not inconveniently written also thus:

$$\frac{V}{S} \cdot \frac{i'}{\tau} = - \frac{V}{S} \cdot \frac{x'}{\tau}; \quad \dots \quad (75.)$$

in using which abridged notation, we must be careful to remember, respecting the characteristic  $\frac{V}{S}$ , of which the effect is to form or to denote the *quotient of the vector part divided by the scalar part* of any quaternion expression to which it is prefixed, that *this new characteristic of operation is not (like S and V themselves) distributive relatively to the operand*. The vector denoted by the first member of (74.) or of (75.) is a line perpendicular to the plane of  $i'$  and  $\tau$ , that is to the tangent

plane of the ellipsoid; and its length is the trigonometric tangent of the angle of rotation in that plane from the direction of the line  $\tau$  to that of the line  $t'$ ; while a similar interpretation applies to the second member of either of the same two equations, the sign  $-$  in that second member signifying here that the two equally long angular motions, or rotations, from  $\tau$  to  $t'$ , and from  $\tau$  to  $x'$ , are performed in opposite directions. Thus the vector  $\tau$ , which touches a line of curvature, coincides in direction with the bisector of the angle in the tangent plane between the projections,  $t'$  and  $x'$ , of the cyclic normals thereupon; or with that other line, at right angles to this last bisector, which bisects in like manner the other and supplementary angle in the same tangent plane, between the directions of  $t'$  and  $-x'$ : since  $x'$  may be changed to  $-x'$ , without altering essentially any one of the four last equations between  $\tau, t', x'$ . Those two rectangular and known directions of the tangents to the lines of curvature at any point of an ellipsoid, which were obtained by the process of article 53, are therefore obtained also by the process of the present article; which conducts, by the help of the geometrical reasoning above indicated, to the following expression for the system of those two tangents  $\tau$ , as the symbolical solution (in the language of the present calculus) of any one of the four last equations (72.),..(75.):

$$\tau = t'(\mathbf{U}t' \pm \mathbf{U}x'); \quad \dots \dots \dots \quad (76.)$$

where  $t'$  is a scalar coefficient.

The agreement of this symbolical result with that marked (62.) may be made evident by observing that the equations (68.) give

$$t' = \nu^{-1} \mathbf{V} \cdot \mathbf{v}; \quad x' = \nu^{-1} \mathbf{V} \cdot \mathbf{v}x; \quad \dots \dots \dots \quad (77.)$$

so that if we establish, as we may, the relation

$$tt' = (\mathbf{T}\nu)^{-1}, \quad \dots \dots \dots \quad (78.)$$

between the arbitrary scalar coefficients  $t$  and  $t'$ , which enter into the formulæ (62.) and (76.), those formulæ will coincide with each other. And to show, without introducing geometrical considerations, that (for example) the form (73.) of the recent condition relatively to  $\tau$  is symbolically satisfied by the expression (76.), we may remark that this expression, when operated upon according to the *general rules* of this calculus, gives

$$\begin{aligned} \mathbf{T}x' \cdot \mathbf{V} \cdot t' \tau &= \pm t' \mathbf{V} \cdot t' x'; \\ \mathbf{T}x' \cdot \mathbf{S} \cdot t' \tau &= t'(-\mathbf{T} \cdot t' x' \pm \mathbf{S} \cdot t' x'); \end{aligned} \quad \left. \right\} \quad (79.)$$

$$\mathbf{T}t' \cdot \mathbf{V} \cdot \tau x' = t' \mathbf{V} \cdot t' x'; \quad \mathbf{T}t' \cdot \mathbf{S} \cdot \tau x' = t'(\mathbf{S} \cdot t' x' \mp \mathbf{T} \cdot t' x'); \quad \left. \right\}$$

and that therefore the two members of (73.) do in fact receive,

in virtue of (76.), one common symbolical value, namely one or other of the two which are included in the ambiguous form

$$\frac{V.\sqrt{x}}{S.\sqrt{x} \mp T.\sqrt{x}}; \dots \dots \dots \quad (80.)$$

respecting which form it may not be useless to remark that the product of its two values is unity.

[To be continued.]

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**LXXVI. Contributions to the Chemical History of Gun-Cotton and Xyloidine. By Mr. JOHN HALL GLADSTONE, of University College, London\*.**

AT the commencement of the present year, having perceived that considerable doubt rested on the ultimate composition of gun-cotton, I undertook a series of experiments with a view to ascertain it, if possible; and during my investigation my attention was drawn to various papers that appeared on the subject, where I found contradictory accounts, not only of the results of analysis, but also of the action of various reputed solvents. The experiments detailed below, although they are far from exhausting the subject, may serve to explain some of these anomalies, and to point out a few facts, which, as far as I have been able to learn, have not been hitherto noticed.

The cotton employed was that used by jewellers, well-carded, perfectly white, and free from imperfections. An analysis of the substance by combustion with oxide of copper in a stream of oxygen yielded the following results:—

Cotton employed . . . . .	3·16	grs.
Carbonic acid produced . . . . .	5·14	...
Water produced . . . . .	2·06	...

These proportions are,—

Carbon . . . .	44·37
Hydrogen . . . .	7·24
Oxygen . . . .	48·39
	100·00

Lignine calculated from the formula C<sub>24</sub>H<sub>20</sub>O<sub>20</sub>:—

Carbon . . . .	44·44
Hydrogen . . . .	6·17
Oxygen . . . .	49·39
	100·00

The excess of hydrogen doubtless arises from moisture absorbed by the oxide of copper during the unavoidable delay in mixing it with the cotton.

\* Communicated by the Chemical Society; having been read June 7, 1847.

This cotton, which may be considered as pure lignine, was steeped until thoroughly wetted in a mixture of nitric acid of spec. grav. 1·502, and nearly an equal bulk of strong sulphuric acid, then well-washed with water, and dried at a temperature not exceeding 212°. In one instance 38·38 grs. of cotton became 66·84 grs., being an increase of 28·46 grs., or 74·15 per cent. In a second experiment 59·3 grs. of cotton gave an increase of 43·7 grs., or 73·7 per cent. The gun-cotton, or pyroxyline, thus produced resembled the original cotton in physical properties very closely, and exploded at about 370°, producing no smoke and leaving no residue.

The action of various solvents and reagents upon this substance was found to be as follows:—It is absolutely insoluble in pure water, and nearly so in strong alcohol, æther, whether hydrated or anhydrous, and in a mixture of æther with  $\frac{1}{10}$ th part of alcohol; but acetic æther instantly destroys its fibre, and dissolves it in large quantity. The solution yields on spontaneous evaporation a white powder of the same weight as the original pyroxyline, but I have found it very difficult to drive off the last traces of the solvent. The action of sulphuric acid upon it differs from that exerted upon unaltered cotton; for, while the latter is instantly dissolved by the strong acid, and charred upon a slight elevation of temperature, pyroxyline dissolves with difficulty unless the acid be warmed, evolving at the same time nitric oxide and other gases, and not being charred even upon boiling. With the aid of heat it dissolves immediately in a solution of potash. By means of these three last-mentioned tests I was able to prove the absence of any unaltered cotton in the product under examination. The action of other reagents upon gun-cotton was not so decided; it was dissolved, but not without long boiling, by ammonia, the alkaline carbonates, hydrochloric acid, acetic acid, both glacial and dilute, and weak sulphuric acid. These solutions, as well as the two preceding, contained nitric acid; nothing could be precipitated from them by dilution or neutralization; and when evaporated they yielded only a dark brown amorphous matter. It is evident that none of these reagents restore the lignine in its original condition; and they do not afford any means of ascertaining whether the compound contains the elements of nitric or hyponitric acid.

As there exists a great discrepancy in the accounts given of the increase of weight in making gun-cotton, I examined whether the length of time it was immersed in the acid liquor, or the proportions of the acids employed, were the cause. The length of immersion I found to produce no alteration; but

upon employing two measures of sulphuric acid to one of nitric acid, I obtained a product resembling in all respects ordinary pyroxyline, yet 42.77 grs. gave an increase of only 24.31 grs., or 56.84 per cent. Upon a repetition of this experiment I found the increase to be 59.93 per cent., and again 70.6 per cent. Suspecting from the disparity of these results that something might be dissolved in the acid liquor, I immersed 6.7 grs. of cotton in a large quantity of the mixed acids, but it increased 4.9 grs., or 73.1 per cent. Perceiving that I had obtained an opposite effect to that anticipated, I treated 12.64 grs. of cotton with just sufficient of the mixture to wet it thoroughly: the fibre was evidently somewhat destroyed; the increase in weight was only 6.54 grs., or 51.74 per cent., and the acid liquor squeezed from the cotton, neutralized with ammonia, evaporated to dryness, and heated, gave abundant evidence of organic matter being present. Lest however it might be supposed that the whole had not been converted into pyroxyline, it was treated again with the mixed acids, but that produced an increase of only 0.12 gr. The action of various solvents confirmed its identity with ordinary pyroxyline, while its solubility in potash proved that the transformation had been very nearly complete. A repetition of the experiment gave similar results. It thus appears that the small increase in weight in the preparation of pyroxyline takes place when there is not sufficient nitric acid present to prevent the peculiar action of the sulphuric acid, namely, that of dissolving and altering it. When however the increase amounted to about 74 per cent., I was never able to detect the presence of oxalic acid or other organic matter in the acid liquor; and as no gas is evolved during the preparation of pyroxyline, it may be concluded that there is no secondary product containing carbon.

Subsequently, when Dr. Schönbein had specified *his* method of making gun-cotton, I treated 18.78 grs. of cotton with a mixture of three parts of sulphuric acid and one of nitric acid, sp. gr. 1.5, following his directions. The result was 32.92 grs. of a substance similar to that produced in former experiments, being an increase of 75.20 per cent. On another occasion 80.95 grs. of cotton gave an increase of 61.10 grs., or 75.47 per cent. The action of solvents and reagents confirmed the identity of this pyroxyline with that obtained in my previous experiments, and I was equally able to establish the absence of any secondary product containing carbon.

In determining the ultimate composition of pyroxyline several precautions were found to be necessary. In the ana-

lyses recorded below it was cut into small pieces, and, after the weight was taken, mixed carefully with oxide of copper. To prevent its caking together the admixture of a little asbestos was found useful. This was introduced into a long combustion-tube, then some fresh oxide of copper, and upon it again some fused into lumps so as to fill the whole bore for about 7 inches. Lastly, was added a mixture of copper turnings and reduced copper for about 9 inches. The combustion conducted cautiously in the usual manner gave the following results; the pyroxylite burnt in the sixth experiment having been prepared by Schönbein's method.

	I.	II.	III.	IV.	V.	VI.
Pyroxylite employed	4·09	4·61	3·57	4·85	4·55	2·905
Carb. acid produced	4·20	4·52	3·42	4·88	...	2·84
Water produced . .	1·19	1·36	...	...	1·34	0·87

Hence in 100 parts,—

	I.	II.	III.	IV.	V.	VI.
Carbon .	27·90	26·74	26·10	27·44	...	26·65
Hydrogen	3·22	3·27	...	...	3·27	3·32

In order to determine the amount of nitrogen the differential mode was adopted, as the method of MM. Will and Varrentrapp is inapplicable to substances containing this element in so highly oxidized a state. The same precautions were taken as in the estimation of carbon; and the collected gases gave the following results after due correction for barometrical pressure :—

	I.	II.	Another specimen.
Carbonic acid .	25·0	38·5	23·9
Nitrogen . . .	5·5	8·5	5·1

These proportions are,—

Nitrogen.	Carbonic acid.
1	: 4·55
1	: 4·53
1	: 4·68

The volumes of the gases represent respectively equivalents of carbon and nitrogen, and since no secondary product is formed in the conversion of lignine into pyroxylite, the 24 equivalents of carbon in the former must be found in the latter. This will give the following ratio in equivalents of carbon and nitrogen according to the three experiments above cited :—

	I.	II.	III.
Carbon . . . .	24·0	24·0	24·0
Nitrogen . . . .	5·28	5·3	5·12

or 24 : 5, which accords with the proportions assigned by M. Pelouze \*.

The formula which best agrees with these results is the following :—  $C_{24} \left\{ \frac{H_{15}}{5 NO_4} \right\} O_{20}$ , which reckoned to 100 parts, gives—

Carbon . . . . .	26·23
Hydrogen . . . . .	2·73
Nitrogen . . . . .	12·75
Oxygen . . . . .	58·29

In order to compare pyroxyline with xyloidine, I treated starch with fuming nitric acid until the whole was converted into a gelatinous mass. The addition of water then threw down a white powder, which was subsequently well-washed and dried. The iodine test proved the absence of all unaltered starch. The xyloidine thus obtained explodes at about 360°, leaving a carbonaceous residue. It is slightly soluble in æther, with which it is capable of forming a peculiar compound not yet investigated; more so in alcohol, but most of all in æther mixed with a small proportion of alcohol, or in acetic æther. It is dissolved by strong sulphuric acid without the aid of heat, and by boiling solutions of potash, ammonia, hydrochloric acid and dilute sulphuric acid. These solutions contain nitric acid, and nothing is precipitated from them by dilution or neutralization. Xyloidine is also soluble in strong acetic acid, or in nitric acid, whether fuming or of sp. gr. 1·25, but is reprecipitated from either by dilution.

It was also found that nitric acid of ordinary strength (sp. gr. 1·45) answered equally well in the preparation of this substance; but when acid of sp. gr. 1·41 was employed no such result was obtained. Starch treated with a mixture of equal measures of nitric and sulphuric acids produced a substance of greater combustibility, and more closely resembling pyroxyline, but differing from it in being soluble in glacial acetic acid, and in a mixture of æther with one-tenth part of alcohol, as also in the action that acetic æther exerts upon it. Xyloidine also when subjected to the mixed acids gave a product identical with the above, as far at least as the action of solvents can prove.

Xyloidine burnt by means of oxide of copper, with the usual precautions, gave the following results. The substance employed in the third experiment was made from arrow-root.

\* *Comptes Rendus*, Jan. 4.

	I.	II.	III.
Xyloidine employed . . .	4·77	5·23	6·75
Carbonic acid produced . . .	5·30	5·91	7·87
Water produced . . .	1·84	1·96	2·80

Hence in 100 parts,—

	I.	II.	III.
Carbon . . .	30·30	30·82	31·79
Hydrogen . . .	4·28	4·16	4·60

In the determination of nitrogen by the differential method the proportions of the gases obtained were,—

	I.	II.	III.
Carbonic acid . . .	70·7	53·4	53·8
Nitrogen . . .	10·6	6·9	8·0

These are in the proportion of—

	I.	II.	III.
Carbon . . .	24·0	24·0	24·0
Nitrogen . . .	3·59	3·10	3·57

These numbers suggest the simple substitution product  $C_{24} \left\{ \begin{matrix} H_{17} \\ 3 NO_4 \end{matrix} \right\} O_{20}$ , in which the per-cent age of carbon would be 31·37, and of hydrogen 3·70; yet the amount of nitrogen is somewhat too great, and there is far from being sufficient evidence to prove the definiteness of the substance itself. The wide difference also in the results obtained by various chemists can scarcely be accounted for, except upon the supposition that they have operated upon very different substances.

The solubility of xyloidine in nitric acid led me to examine whether any alteration could be effected upon pyroxylene by similar means. The most dilute acid which I found to have any effect upon it in the cold was that of sp. gr. 1·414; but the alteration took place by means of this only after long standing, and but to a slight extent. Nitric acid of sp. gr. 1·45 however is capable of dissolving pyroxylene, and alters both its composition and properties, as will be presently described; whilst fuming nitric acid has not the slightest effect upon it. The new product just mentioned is acted upon somewhat differently by various solvents, according to whether it exists in a fibrous condition, or in powder as precipitated from solution; yet I have found by experiment that no alteration in weight is effected by this change of condition. When in fibre it is slightly soluble in strong alcohol, æther, a mixture of æther with one-tenth part of alcohol, and acetic æther; but when in the pulverulent state it is very soluble in these menstrua, and in glacial acetic acid. In either con-

dition it leaves a carbonaceous residue on combustion, is dissolved by nitric acid, whether of sp. gr. 1·25 or 1·5, and reprecipitated upon dilution. Strong sulphuric acid also dissolves it in the cold, and chars it at a temperature below 180°. These two last properties show that the original pyroxyline was perfectly free from admixture with this new substance.

There occurs a considerable decrease of weight through this transformation. In the first experiment 32 grs. of substance operated upon gave 25·82 grs. of the new product; in the second 43·64 grs. of the one yielded 34·68 of the other. Now assuming the increase in the preparation of pyroxyline to be 75 per cent., the weight of the new product above that of the original cotton would be, as calculated from these figures, 41·1 and 39·05 per cent.

When this new product, whether in the fibrous or the pulv-erulent condition, was treated with a mixture of equal parts of nitric and sulphuric acids, it increased considerably in weight, and the resulting substance had all the properties of pyroxyline as prepared in the usual manner. 11·16 grs. of the one yielded 13·56 grs. of the other; the quantity that should theoretically have been obtained, calculating it from the decrease in making the new product, is 13·84 or 14·04 grs. Again, 12·35 grs. of the substance as precipitated from solution gave 15·75 grs., the theoretical amount would have been 15·31 or 15·54 grs. This result proves the distinctness of the new product from xyloidine, a fact that could not have been ascertained from the action of the before-mentioned solvents.

Whilst engaged in obtaining these results, I also examined the action of nitric acid of various degrees of strength upon pure cotton. By treating it with nitric acid of sp. gr. 1·5 I obtained a product evidently different from gun-cotton, but as it did not appear to be homogeneous throughout, I passed on to investigate the action of a weaker acid. That of sp. gr. 1·45 gave a substance which proved to be identical with the product of the action of the same acid upon pyroxyline. Upon a repetition of the experiment 68·54 grs. increased in weight 14·61 grs., or 21·31 per cent.—a smaller increase than might have been anticipated, but which may easily be accounted for by the fact that the whole cotton had not been transformed, as was proved by a considerable portion being left undissolved by a boiling solution of potash. Nitric acid of sp. gr. 1·414 produced the same alteration, but only to a small extent, and after long standing. 23·75 grs. of cotton soaked in nitric acid of sp. gr. 1·516 became a hard mass,

and increased in weight 13·49 grs., or 56·8 per cent.; the action of various solvents upon the resulting substance indicated that it was a mixture of pyroxylene and the new product. On another occasion, when the transformation by means of nitric acid sp. gr. 1·47 proved to be complete, 29·52 grs. of cotton increased 9·51 grs., or 32·89 per cent. But in order to obtain a substance sufficiently pure for analysis 16·29 grs. of cotton were treated with enough nitric acid to dissolve the whole; the new product was precipitated by dilution, and the increase in weight was found to be 5·34 grs., or 32·78 per cent. In these instances there occurred a secondary product containing carbon not precipitable by water.

When this was subjected to combustion with oxide of copper, the following results were obtained:—

	I.	II.	Another specimen.
Substance employed .	3·15	2·985	3·165
Carbonic acid produced	3·58	3·39	3·55
Water produced. . .	1·00	1·01	1·14

Hence in 100 parts,—

Carbon .	30·99	30·97	30·59
Hydrogen	3·52	3·75	4·00

I was unable to obtain any very accurate estimation of nitrogen by the differential method: the results most to be depended upon were—

Carbonic acid . . .	120·7	76·7
Nitrogen . . . .	13·6	8·3

In the proportion of

Carbon . . . .	24·0	24·0
Nitrogen . . . .	2·7	2·6

These numbers lead me to think that there are 3 equivalents of nitrogen in the compound, especially as I observed during the combustion that the substance became charred even 1 or 2 inches beyond the glowing charcoal, which will account for the deficiency of nitrogen when compared with the carbonic acid. Hence the composition of the new product coincides very nearly with that calculated from the

formula  $C_{24} \left\{ H_{17} \atop 3 NO_4 \right\} O_{20}$ , namely,

Carbon . . . .	31·37
Hydrogen . . . .	3·70
Nitrogen . . . .	9·15
Oxygen . . . .	55·78
	100·00

Under this supposition the increase in weight in the preparation would be 41·66 per cent.; very similar to that calculated from the results obtained by the action of nitric acid, sp. gr. 1·45, on pyroxylene, namely, 39·05 and 41·1 per cent.

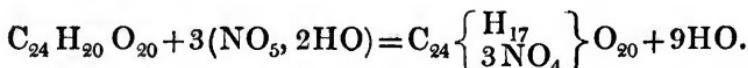
In order to add an additional proof of the identity of the two substances obtained by the action of nitric acid of sp. gr. 1·45 on cotton and on pyroxylene, and also of the fact that pyroxylene is reproduced by the action of mixed sulphuric and nitric acids upon the new product, the experiment was repeated with a portion of the substance made from pure cotton: the result was pyroxylene. In the transformation 26·56 grs. became 38·04: now these 26·56 grs. were produced from 21·81 grs. of the original cotton; hence the increase upon the cotton itself would be 16·23 grs., or 74·4 per cent., coinciding with the amount usually obtained in the preparation of pyroxylene.

I. From these results it appears that in the treatment of woody fibre by nitric acid raised to its highest degree of strength by the addition of sulphuric acid, 5 equivalents of the acid combine with 1 of lignine to produce pyroxylene, displacing 5 equivalents of the elements of water, as indicated by the formula  $C_{24} \left\{ \frac{H_{15}}{5NO_4} \right\} O_{20}$ . The amount per cent. of carbon and hydrogen hence deduced closely agrees also with that assigned by Mr. Ransome \* and M. Pettenkofer †.

	Calculated.	Ransome.	Pettenkofer.
Carbon . .	26·23	26·28	26·26
Hydrogen . .	2·73	3·16	2·75

In this case the synthetical experiment would give an increase of 69·44 per cent.—nearly the amount obtained in the best experiments. My own analyses however have yielded a somewhat larger amount of carbon.

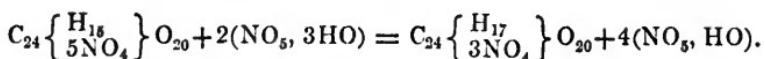
II. If lignine be treated with nitric acid combined with more than 1 equivalent of water, another compound is produced, containing a smaller proportion of the elements of nitric acid, most probably  $C_{24} \left\{ \frac{H_{17}}{3NO_4} \right\} O_{20}$ , and very closely resembling, but not identical with, pyroxylene.



Also if pyroxylene itself be treated with nitric acid containing 3 equivalents of water, the same compound results:

\* Phil. Mag., January 1847.

† Pharmaceutisches Central Blatt, Dec. 30th, 1846.



And this transformation may be reversed.

Whilst completing my examination of this substance, my attention was drawn to the communication of M. Payen in the *Comptes Rendus* of Jan. 25th, where some properties of "coton hypoazotique" are described. It is possibly the same; yet, in order to express its distinctness from pyroxylene, I would propose as the appellation of my substance cotton-xyloidine.

Before concluding I would acknowledge my obligations to several chemists whose published investigations on the same subject have suggested many of my experiments, and more particularly to Professor Fownes for the valuable advice with which from time to time he has favoured me.

## LXXVII. Proceedings of Learned Societies.

### ROYAL ASTRONOMICAL SOCIETY.

[Continued from p. 389.]

June 11, ON the Opinion of Copernicus with respect to the 1847. Light of the Planets. By Professor De Morgan.

The common story is, that Copernicus, on being opposed by the argument that Mercury and Venus did not show phases, answered that the phases would be discovered some day. The first place in which I find this story is in Keill's Lectures. It is also given by Dr. Smith, in his well-known Treatise on Optics, by Bailli, and by others. But I cannot find it mentioned either by Melchior Adam or Gassendil, in their biographies of Copernicus; nor by Rheticus, in his celebrated *Narratio*, descriptive of the system of Copernicus; nor by Kepler, nor by Riccioli, in their collections of arguments for and against the heliocentric theory; nor by Galileo, when announcing and commenting on the discovery of the phases; and, what is most to the purpose, Müller, in his excellent edition of the great work of Copernicus, when referring to the discovery of the phases of Venus, as made since, and unknown to, Copernicus, does not say a word on any prediction or opinion of the latter.

This story may then be rejected, as the gossip of a time posterior to Copernicus. If we try to examine what the opinion of Copernicus on this matter really was, a point of some little curiosity arises. It depends on one word, whether he did or did not assert his belief in one or other of these two opinions,—that the planets shine by their own light, or that they are saturated by the solar light, which, as it were, soaks through them. I support the affirmative: that is to say, I hold it sufficiently certain that Copernicus did express himself to the effect that one or the other of these suppositions was the truth.

If we take the first edition of the work *De Revolutionibus*, which

was printed from the manuscript furnished by Copernicus himself, there is little doubt about the matter. There are but two passages which bear or can bear upon the question. The first is in the *ad lectorem*, in which the writer (Osiander, though even Delambre make him Copernicus) asks whether any one acquainted with geometry or optics can receive the Ptolemaic epicycle then used to explain the motion in longitude of Venus? But the meaning of the allusion to optics is explained in the next sentence, by a reference (and by no means a fortunate one) to the changes of apparent diameter of Venus derived from that epicycle; changes which, as they made the perigean diameter more than four times as great as the apogean, were assured to be falsified by common experience. The second passage is the one on which this discussion must turn. In book i. chap. x., after noting that some had theretofore believed Mercury and Venus to come between the earth and sun, he mentions the difficulty arising from the absence of the remarkable phase, which we now call the transit over the sun's disc. He describes the opinion just mentioned favourably, referring, not to his own view, but to that of those others who had held it. This is not an uncommon idiom: persons advocating an unpopular opinion are very apt to describe the maintainers of it in the third person, though themselves be of the number. But when he comes to describe what he takes to be the necessary consequence of the opinion, he lapses into the first person as follows:—"Non ergo fatemur in stellis opacitatem esse aliquam lunari similem, sed vel proprio lumine, vel solari totis imbutas corporibus fulgere, et idcirco solem non impediri . . . ."

These are the words of the first edition (Nuremberg, 1543). That Copernicus could have answered any objection, either by word or writing, is impossible, since he drew his last breath within a few hours of the time when, not able to open it from weakness, he saw the first printed copy. The second edition (Basle, 1566) is usually said to have been edited by Rheticus. The reason of this is that the name of Rheticus appears in the title-page. But this appearance only arises from the *Narratio*, &c. of Rheticus being added to the edition; and it is only the description of this edition which brings Rheticus into the title-page. There is no mark whatever of his having been the editor; and as the work was printed at Basle, where I cannot find that Rheticus ever sojourned, and as the latter was deeply engaged at the time in his enormous trigonometrical calculation, some proof of his editorship must be given before it is admitted. As the point is of importance, I will notice, that unless Rheticus had made some stay at Basle, it is very unlikely he should have edited a work printed there. He did not edite the first edition, only because it was found convenient to print it at Nuremberg instead of at Wittemberg; and it was accordingly entrusted to Osiander. Now, if ever there were a connexion between two men, and between one of them and the book of the other, which made it desirable and even necessary that the first should edite the second, it was the case of Rheticus and the first edition of the *De Revolutionibus*, &c.; and yet no arrangement could be made by which the sheets printed at

Nuremberg could be revised at Wittemberg. It is very unlikely, then, that Rheticus should have edited the second edition, when, as far as we know, a similar impediment existed.

The third edition, by Müller (Amsterdam, 1617), has no authority as to the text above that of the second.

Now both the second and third editions change the word *fatemur* into *fatentur*, thus causing Copernicus to throw the opinion in question upon his predecessors, instead of directly making it his own. Not that it would be conclusive, even if the emendation were adopted : for, as I have said, Copernicus is evidently speaking with approbation of the opinions which he describes ; and it would be difficult to say why *comperiunt* or *putant* in one sentence should imply approbation, and *fatentur*, in the next, should be at least disavowal, if not disapprobation. If Rheticus, who knew the mind of Copernicus better than any one, had been the editor, I can conceive that stress ought to be laid upon the change of the first into the third person as an emendation ; that is, I should be somewhat staggered by Rheticus having thought it necessary to make such an alteration.

But, Rheticus not being in the question, as I think, for the reasons given above, the next best authority on an opinion of Copernicus is Galileo. Now the latter, in speaking of the phases of Venus, expressly attributes to Copernicus the maintenance of one of the two alternatives,—that the planet is either self-luminous or perforated by the solar rays. Of these alternatives, he says, in his letter to Velser (Works, vol. ii. pp. 88, 89), "Al Copernico medesimo convien amettere come possibile, anzi pur come necessaria una delle dette posizioni." And that such was the opinion of Copernicus is also assumed by the writer of the note on the *Sydereus Nuncius* in the volume just mentioned, and by others, even down to our own time ; as by Mr. Drinkwater Bethune, in his life of Galileo. In fact, with the exception of the unsupported story mentioned at the beginning of this paper, there is nowhere, that I can find, anything against my conclusion. And it is to be remembered, that Copernicus nowhere shows any of that acumen in matters of physics, apart from mathematics, which has often enabled the cultivators of the former to make steps more than proportionate to their knowledge of the latter. Ptolemy, the great promoter of the old theory, and Copernicus, its destroyer, were both mathematicians in a peculiar sense ; Ptolemy being far the more sagacious in questions of pure experiment. Their grounds of confidence are mathematical ; and Copernicus, in particular, dares to face his own physics (for there is no reason to suppose he was beyond his age in mechanical philosophy) with reasons drawn entirely from probabilities afforded by mathematics.

There is much reason to regret the practice of associating with the names of those who have led the way in great discovery the glory which is due to their followers. The disadvantage is twofold. In the first place, it introduces into the history of science an index error of from one to two centuries ; secondly, those who come to in-

quire are disappointed to find that they must lower their opinion of great men, and are perhaps led to do it to a greater extent than justice requires. Our usual popular treatises speak of Copernicus as if, besides himself, he had in him no inconsiderable fraction of Kepler, Galileo, Newton and Halley. What is a person to think who comes from those histories to actual investigation, when he finds in Copernicus himself the immovable *centrum mundi* (only reading sun for earth) of the Ptolemaists, their epicycles, and a suspicion, at least, of the solid orbs?

On the Formation and Application of Fine Metallic Wires to Optical Instruments. By Mr. Ulrich.

Dr. Wollaston, in the Philosophical Transactions for 1813, proposed a method of forming wires of gold or platinum of any degree of tenuity. The discovery does not appear to have been much used, owing, as Mr. Ulrich supposes, to the difficulty of application.

Mr. Ulrich forms the fine wire by inserting a gold or platinum wire in the centre of a silver cylinder of much larger dimensions, which is afterwards drawn out by the usual process. When the silver wire has been sufficiently extended, Mr. Ulrich cuts it into short lengths and attaches platina rings to each end. The rings are hooked upon a hooked fork, and the whole is plunged into heated nitric acid, when the silver coating is dissolved.

The artist may now wire his cell according to his fancy. Mr. Ulrich's plan seems to be, to hold one end by an overplate; then to allow the wire to be stretched by its platina ring, and to fix the other overplate. He recommends using a cell of the same material as the wire, as, otherwise, a difference of expansion might break or slacken the wires.

On the properties of Rock as a foundation of the Piers of Meridian Instruments, with an Account of the Detection of a hitherto unsuspected Cause of Error in the Edinburgh Transit. By Professor C. P. Smyth.

Some years ago doubts were expressed of the fitness of a rock foundation for an observatory. It does not appear that any experiments were made, or that any reason was adduced beyond this, that as tremor was unfavourable to the performance of large telescopes, and as rock was more capable of transmitting tremors than less compact material, therefore rock was to be avoided when choosing a site for an observatory. The author or authors of this opinion were probably but ill-acquainted with the mode of working an observatory, or the requisites for obtaining accuracy in meridian observations; yet it is certain that an undue importance was attached in some cases to these very idle surmises. At the present time it is not likely that any intelligent person would be misled by such authorities, and it is therefore unnecessary to mention here the mischief they have caused\*. It is to be wished that the founders of future observatories,

\* The effect of tremor on a telescope is probably familiar to every reader of this notice. It causes a sort of burr round the object, and destroys the sharpness of outline and definition. This is probably more injurious in reflecting than in refracting telescopes; but we may fairly doubt whether it

who can command a rock foundation, should make use of their good fortune; and that those who cannot, would look carefully to the possible effects of moisture, which are probably more extensive, and vary more rapidly, than those of temperature.

The observatory of Edinburgh is placed on the Calton Hill. This is chiefly of a porphyritic formation. The apex was blasted away to obtain a level area, on which the observatory was erected. The site of each pier was cut away until a sound part of the rock was arrived at (it was not necessary to go deeper for this purpose than six or nine inches), when the exact size of the foundation was at once marked out and the space carefully levelled. The foundation stone was also carefully smoothed, and then laid in its place with milk of lime. As the foundation and stone were both rather hollow, except for three inches at the outer edge, which was polished, the fitting was very perfect. There are no vertical joints, and each stone was laid in the same manner as the foundation stone. As one of the principal thoroughfares of Edinburgh runs about 100 feet below, and only 300 feet distant from, the observatory, tremors were confidently predicted by the alarmists. Professor Henderson, however, found none, nor any interruption to his observations in mercury. Professor Smyth adds that he finds no annoyance from the railroad about 300 feet below, and at a horizontal distance of 500 feet.

So far the observatory founded on a rock came out victoriously from its ordeal, but Professor Henderson, in the course of his work, found a well-marked annual variation of the *level* of the transit, which he attributed to the expansion of the rock. This variation seemed so intimately connected with temperature that he latterly took his factor for level correction from the thermometer, having found a constant agreement between this and the indications of the spirit level. The maximum of this change amounted to between  $0^{\circ}.2$  and  $0^{\circ}.3$  in the value of the level factor, and the variations were tolerably regular.

On computing the azimuthal factors for 1841, Professor Smyth

is more felt on solid than on loose foundations. In a *standard* observatory, where observations are made principally in the meridian, tremor scarcely affects the *accuracy* of observation at all, unless it is so excessive as to change the position of the microscopes, piers, &c. Now this is obviously the least likely to happen when the foundation is on rock; the tremors are propagated through the substance, without in any respect altering its form. Sudden and discontinuous changes, which obey no law, are those only which are to be feared in a well-directed observatory. Tremor is chiefly objectionable as disturbing the mercurial horizon, which, however, is now mostly used as a verification, not as the ordinary mode of observing; and when this inconvenience only occurs occasionally, it can generally be avoided or palliated by a little contrivance or foresight. Unless the *adjustments* are kept in a fluctuating and uncertain state by occasional small oscillations (and we believe no careful experiments have been directed to this point), they are minor evils. The experience of the Oxford and of the Edinburgh Observatory is, so far as it goes, conclusive against any danger from moderate exposure to tremors in a well-founded and well-managed observatory.—S.

was very much disturbed on finding variations, which sometimes altered the factor as much as  $0^{\circ} \cdot 3$  in a day, and more than  $1^{\circ} \cdot 0$  in the course of the year. These changes in azimuth had been remarked by Professor Henderson, and were attributed to the irregular action of the counterpoises, which were consequently removed. On a comparison of these errors with the indications of thermometers plunged in the rock there were apparent marks of correspondence.

There are several thermometers inserted at different depths in the rock near the observatory, which had been carefully observed in the year 1841\*. The indications of these thermometers were projected on paper, and the curves thus formed compared with a curve traced according to the course of the azimuthal deviation. It was thus made evident, that the curve of azimuthal deviation, though having, like the other curves, an annual maximum, did not otherwise resemble the curves belonging to the deep-seated thermometers at all; and, in fact, it came nearest the curve traced out by the thermometer attached to the barometer and by the free thermometer exposed to the outer air. Hence the cause of the deviation was not to be looked for in the effect of temperature on the foundations or on the massive transit piers, but on smaller parts more readily affected, such as the metallic mounting. These were accordingly examined. In the azimuthal Y, the construction was found to be much as usual, but the artist has adopted an adjustment for the vertical Y, which seems liable to suspicion. There are two vertical screws applied from below; one, pushing, on the north side of the middle, and the other, pulling, at the south side. The Y is prevented from turning in a vertical plane by jamming horizontal screws, which press a plate against the north face of the Y so as to bring the whole tightly against a stopping-piece, which blocks the south face. Professor Smyth's present opinion is, that the effect of expansion on the two screws, which are in contrary states of constraint, is to alter the adjustment; certainly the arrangement looks unmechanical. In the ordinary mode of construction, in this country at least, the elevating Y is either raised by one central screw, or by two screws, one on each side of the centre; in which case a drawing-screw may be placed at the centre. There is thus no tendency to twist, and the side-plates which confine the Y laterally have to exert little restraining force. Professor Smyth has communicated with MM. Repsold, the makers of this magnificent instrument, and is awaiting their reply before adopting any remedy†.

\* Some years ago, Professor J. D. Forbes had four thermometers sunk in the rock with their bulbs at the depths of 24, 12, 6, 3 French feet and a fifth on the surface merely covered with sand.

† Sudden and lawless changes in azimuth forbid independent determinations of the azimuthal deviation (which are also the best), viz. from the consecutive semidiurnal transits of circumpolar stars. The possessor of an imperfectly mounted instrument must content himself with assuming the fundamental places of his close circumpolar stars, and determine his azimuthal error from each of them. This will, with proper caution, be found quite sufficient for objects not too near the pole, especially when the clock-error stars are pretty numerous, and situated above and below the object to be determined.

### LXXVIII. *Intelligence and Miscellaneous Articles.*

ON OSMIAMIC ACID. BY MM. J. FRITZSCHE AND H. STRUVE.

**W**HEN caustic ammonia is added to a solution of osmic acid in excess of potash, the deep orange colour of the liquid becomes rapidly a bright yellow, and a new salt is produced and separated, either immediately or by evaporating the liquid at a gentle heat, which is a yellow crystalline powder.

The formation of this new compound does not necessarily depend on the presence of potash or any other oxide, but uniformly upon that of ammonia; the ammoniacal salt is, however, subject to alteration, and decomposes during evaporation. It is better therefore to cause a basic oxide to intervene.

M. Gerhardt remarks that the formula of the osmiamates which the authors have given requires correction; they agree, he states, with the formula  $OS, O^3 N (M)$ .

The properties of the osmiamates are as follows: they decompose by heat with explosion; and several of them undergo the same decomposition when struck. Among the products of this decomposition are metallic osmium, an osmiate, or a less oxygenated osmic compound. Protosmiamate of mercury volatilizes without explosion, when heated quickly; and it diffuses a strong smell of osmic acid.

Osmiamic acid can be obtained only in solution in water. In order to prepare it, osmiamate of barytes is to be cautiously decomposed by sulphuric acid, or recently prepared and moist osmiamate of silver is to be decomposed by dilute hydrochloric acid. After filtration a bright yellow-coloured solution is obtained, which may be preserved for several days, if it be sufficiently dilute; on the other hand, if too concentrated, it becomes brownish and decomposes with the disengagement of gas, osmic acid is set free, and a black non-explosive substance is deposited which contains osmium.

The same metamorphosis occurs when the weak acid is evaporated over sulphuric acid.

Osmiamic acid not only expels carbonic acid from carbonates, but also decomposes chloride of potassium. In fact crystals of osmiamate of potash are obtained, if a crystal of chloride of potassium with a drop of solution of osmiamic acid be exposed to evaporation on a strip of glass.

Zinc dissolves in solution of osmiamic acid, with the evolution of a little gas; part of the acid is decomposed, and the zinc is covered with a very adherent black deposit, and flocculi appear in the liquid which possess the odour of osmic acid. When all the undecomposed acid is saturated with zinc, the metamorphosis ceases.

In the cold, acids do not decompose osmic acid or the osmiamates: sulphuric, nitric or hydrochloric acid may be added to their solutions without inconvenience; but decomposition readily occurs when heat is applied, and it is rendered apparent by the disengagement of osmic acid and by the brown colour of the liquor; the products vary according to the nature of the acid employed.

Osmiamates are obtained, either directly by the action of osmic acid on a solution of bases in ammonia, as the salts of potash, zinc, and silver, or by precipitating the potash salt by metallic salts, or by decomposing the silver salt by chlorides.

MM. Fritzsche and Struve have stated that these salts yield no hydrogen by analysis. In two experiments the potash salt gave by combustion with oxide of copper only 0·072 and 0·033 of hydrogen; whereas 0·34 are required for one equivalent of hydrogen.

The osmiamates undergo an interesting decomposition by the action of hydrochloric acid. The products vary according to the concentration of the acid. If the potash salt be sprinkled with concentrated acid, energetic action immediately ensues, accompanied with the disengagement of chlorine and probably of its oxide; the hydrochloric acid assumes a fine purple tint, and the crystals of osmiamate of potash are covered with a crust of small red crystals of two different kinds; if the salt employed be powdered, and the action of the hydrochloric acid be long enough continued, all the osmiamate undergoes this change; the nature of which the authors have not hitherto succeeded in explaining.

If dilute hydrochloric acid be added to a solution of osmiamate of potash saturated cold, no decomposition occurs at common temperatures, the metamorphosis taking place only at a higher temperature. It is then more complicated, the liquor temporarily assumes a red and brown tint, and soon emits a smell of osmic acid, which is abundantly disengaged as soon as the liquor is heated to ebullition. If the solution be evaporated to the crystallizing point, as soon as it ceases to emit osmic acid, a mixture of salts is obtained, among which, as shown by the microscope, are hexagonal green tables, green needles, and another red salt, &c. These salts appear to be decomposed by water, for they were not obtainable by solution and recrystallization.—*Journ. de Ph. et de Ch.*, Octobre 1847.

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#### ON THE PREPARATION AND PROPERTIES OF SOME OSMIAMATES. BY MM. FRITZSCHE AND STRUVE.

*Osmiamate of Potash.*—This salt is best prepared by dissolving solid osmic acid in a concentrated solution of caustic potash, with the addition of ammonia during the agitation of the mixture. The solution becomes of a bright yellow tint, and the osmiamate of potash is deposited in the state of a yellow granular powder. The product of the distillation of osmic liquors may also be directly passed into a solution of potash, containing ammonia and properly cooled; the simultaneous distillation of nitrous vapours must be carefully avoided, as they would decompose the osmiamate of potash.

In both cases, the mother-water which has deposited osmiamate of potash is to be evaporated with a gentle heat; carbonate of potash may be used instead of caustic, but not so advantageously; the osmiamate of potash is to be dissolved in a very small quantity of boiling water; on cooling the solution yields small crystals of the salt of a lemon-yellow colour; these crystals are of considerable size

when prepared from a cold saturated solution by spontaneous evaporation, their form being an acute octahedron with a square base.

Osmiamate of potash is much less soluble in alcohol than in water; it dissolves without alteration, and decomposes but very little when the solution is evaporated; it contains no water of crystallization; it may be heated to 356° F. without decomposing, but it becomes brownish and is rapidly decomposed at a higher temperature, with violent projections.

This salt yielded by analysis—

Osmium .....	67·900
Nitrogen .....	4·126      4·820
Potash .....	16·126

M. Gerhardt gives as an amended formula  $\text{OSO}_3\text{N}(\text{K})$ .

*Osmiamate of Soda* is best obtained from the silver salt and chloride of sodium; the crystals are prismatic, contain water of crystallization, and are very soluble in water.

*Osmiamate of Ammonia* is prepared in the same manner. It forms large anhydrous crystals, which appear to be isomorphous with the salt of potash; at 258° F. it decomposes with explosion. This salt is very soluble in water and in alcohol.

*Osmiamate of Barytes* readily crystallizes in yellow brilliant needles of several lines in length. This salt is readily soluble in water, and explodes at about 300° F. It yielded by analysis—

Barytes .....	23·88
Osmium .....	61·07
Nitrogen .....	4·269

the formula according to M. Gerhardt being  $\text{OSO}_3\text{N}(\text{Ba})$ .

*Osmiamate of Ammonia and Zinc* is obtained either by dissolving osmic acid in a solution of a salt of zinc in caustic ammonia, or by mixing a solution of osmic acid in ammonia with the solution of a salt of zinc. A yellow, bright crystalline powder is soon deposited, which is deprived of the mother-water by washings with ammonia.

This compound is very permanent; it may be dried in the air, and remains without losing ammonia. It is nearly insoluble in ammonia, water decomposes it even when cold; when boiled in water it is completely decomposed with the deposition of oxide of zinc, the disengagement of half of its ammonia, and yielding osmiamate of ammonia. Formula according to M. Gerhardt  $\text{OSO}_3\text{N}(\text{Zn})$ ,  $2\text{NH}_3$ .

*Osmiamate of Lead*.—A solution of nitrate of lead is not precipitated by a concentrated solution of osmiamate of potash; after some time some crystals are however formed, which are not sufficiently stable for examination. A solution of acetate of lead gives with the solution of the osmiamates a non-crystalline precipitate, which is at first of a dirty yellow colour, but it soon becomes of a purple tint with the extrication of osmic acid.

If a solution of chloride of lead, or a solution of nitrate of lead with the addition of hydrochloric acid, be added to a solution of osmiamate of potash, a yellow crystalline precipitate is soon obtained, which the authors consider to be a compound of equal equivalents of chloride and osmiamate of lead.

*Protosmiamate of Mercury* forms a bright yellow precipitate ; it is not crystalline, and is insoluble in water ; the perosmiamate of mercury forms prismatic crystals.

*Osmiamate of Silver* is obtained directly by dissolving osmic acid in an ammoniacal solution of a salt of silver, and afterwards super-saturating with nitric acid. It may also be obtained by adding to a solution of osmic acid in ammonia nitric acid in excess at first, and then a salt of silver. It may also be prepared by double decomposition with the salts of silver and soluble osmiarnates.

Osmiamate of silver is a crystalline powder of a lemon-yellow colour ; it is very slightly soluble in water and in cold nitric acid, more soluble in ammonia, and may be combined with it. It may be dried in the dark without blackening, *in vacuo*, over sulphuric acid ; eventually, however, it suffers decomposition, and then gives out osmic acid ; at 176° F. it decomposes suddenly and with violent detonation ; it is also decomposed by percussion, and likewise when sulphuretted hydrogen is passed over the dried salt ; nitric acid decomposes it readily when heated ; the liquor first acquires a brown tint, and gradually becomes colourless with the disengagement of osmic acid.

This salt yields by analysis—

Oxide of silver ..	32·08	32·060	32·13
Osmium .....	55·011		

M. Gerhardt gives as its formula  $\text{OSO}_3\text{N}(\text{Ag})$ .—*Journ. de Ph. et de Ch.*, Octobre 1847.

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#### ON SULPHATO-CHLORIDE OF COPPER,—A NEW MINERAL. BY ARTHUR CONNELL, ESQ.

This mineral occurs in small but very beautiful fibrous crystals, of a fine blue colour, which is pale when the fibres are delicate, but much deeper when they become somewhat thicker. Their form, according to Mr. Brooke, is a hexagonal prism with the edges replaced, thus belonging to the rhombohedral system. They possess considerable translucency, and have a vitreous lustre. On account of the small quantity which he possessed, Mr. Connell was unable to state the specific gravity, hardness, or fracture. Their locality is Cornwall. Mr. Brooke is aware of the existence of only a very few specimens of the mineral : one is in the British Museum.

Like atacamite, this mineral colours the blowpipe flame as well as the simple flame of a candle, of a fine greenish-blue, indicating the presence of chloride of copper. Reduced to powder, and mixed in sufficient quantity with charcoal powder, and then heated in a close tube, it gives decided, although not strongly marked, indications of the presence of sulphuric [sulphurous?] acid by the smell, and partial bleaching of Brazil wood paper, the remainder of the paper being reddened, doubtless by muriatic acid vapours. Alone, in the close tube, it yields a little water, and other appearances resembling those afforded by atacamite. Heated alone on charcoal before the blowpipe, it decrepitates strongly ; but when previously deprived

of the greater part of its water by gentle heat, and then powdered and moistened, and heated on charcoal, it gives no traces of arsenio, although arseniate of copper is associated with it in the specimens. The residue is a dark reddish slag or globule.

The crystals are ngt soluble in boiling water, but dissolve entirely and pretty readily in nitric or muriatic acid, especially by the aid of a gentle heat. The solutions have the colour belonging to copper solutions ; and in the act of dissolving a very few bubbles of gas may be observed to arise, indicating probably the presence of a minute quantity of carbonate. The solutions yield, with barytic salts, a white precipitate insoluble in acids ; and the nitric solution gives, with nitrate of silver, a white and curdy precipitate insoluble in acids or water, but soluble in ammonia. Ammonia in excess, added to the original solution, gives the fine deep blue of copper.

These appearances, in conjunction with the blowpipe reactions, are sufficient to show that the constituents of the mineral are sulphuric acid, chlorine, copper, and a little water ; but Mr. Connell had not sufficient of the mineral to determine the proportions of its constituents. The chloride is apparently more abundant than the sulphate.—Jameson's *Journal*, October 1847.

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#### ON THE FORMATION OF VALERIANIC ACID. BY M. THERAULT.

The author remarks that it has been long known that the oil of potatoes yields valerianic acid under the influence of the caustic alkalies; and it has also been stated that the oil of valerian gave analogous results. M. Therault thought it would be an interesting subject of inquiry to determine in what manner this transformation occurs, and whether it is complete or only partial ; and in the latter case to examine into the nature of the non-acidifiable product ; whether the alkalies directly produced a true chemical reaction on the elements of the oil ; and lastly, whether the intervention of other agents is not requisite to effect the transformation.

In order to resolve these questions, the following experiments were performed, care being taken to operate with oil perfectly deprived of any trace of acid.

1. A portion of oil was mixed with distilled water, and divided into two parts, one of which was exposed to the contact of the air, and the other put into a bottle to prevent its action.

2. Another portion of the oil was mixed with caustic potash, perfectly dry and reduced to powder, and divided as in the preceding experiment.

3. A mixture was prepared of six parts of oil and three parts of potash, previously dissolved in one part of water, and the mixture was divided as in the foregoing experiments.

The following observations were made on these mixtures. After the contact of a month, that portion of the mixture of the first experiment which had been submitted to the action of the air, had become sensibly acid ; in the second portion no change had occurred. In the second experiment no sensible trace of valerianic acid was

produced ; the potash and the oil had nearly retained their original properties.

Circumstances were quite different in the third experiment. The mixture had hardly been made when it became of the consistence of honey, and of a red colour of considerable intensity : perfect saponification might be suspected. M. Bonastre had previously remarked this action of the caustic alkalies on some essential oils, and had proposed it as a means of distinguishing mixtures of them ; and he noticed the partial combination of the oil of valerian with soda. This fact might induce the belief that this oil was a substance of a complex nature ; M. Therault is, however, of opinion that this is not the case, but that the observation of M. Bonastre was derived from the circumstance of the oil which he employed containing valerianic acid, which would explain in this case the partial combination with soda. The author attentively examined the nature of this mixture : it was perfectly homogeneous, and comparable to crotonic soap. Treated with water and suffered to remain undisturbed, the oil soon collected on the surface ; it was separated, and the filtered liquor was saturated with acetic acid. No sensible trace of oil was reproduced, nor was the formation of valerianic acid detected ; it was therefore certain that no chemical action had occurred ; and the name of combination given to this mixture appears to the author to be improper under these circumstances.

M. Therault relies upon this last fact as corroborating the result of the third experiment. The portion of the mixture kept from the contact of the air, underwent no change of properties after one month ; no combination had occurred between the oil and the potash ; no valerianic acid was formed, or at any rate no appreciable quantity.

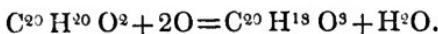
On the contrary, that portion which had been exposed to the action of the air contained valerianic acid, in minute quantity certainly, but it was very appreciable : the matter was slightly decolorized. The action of the air was allowed to continue, and after six months' exposure nearly the whole of the oil had disappeared, and the mixture was almost entirely decolorized, a slight amber tint only remaining.

The decoloration occurred nearly in direct proportion to the quantity of acid formed : the action of the air was however continued, to ascertain whether the whole of the oil could be acidified ; the operation required nearly six months, but it was then complete ; the mixture had assumed the aspect of white, slightly grumous honey ; well-defined crystals of valerianate of potash had formed, and were dispersed throughout the mass. It was covered with a solution of this salt and of potash, without any trace of oil.

It may be concluded from the experiments detailed, that valerianic acid does not pre-exist in valerian root ; that it is entirely the product of the oxidizement of its oil ; that this oxidizement is due to the oxygen of the air ; and that water and the caustic alkalies greatly facilitate this oxidizement. The author also concludes that the caustic alkalies exert no direct action on the elements of the oil ; that they act only by the property which they possess of forming an

intimate mixture with the oil, and exposing it in a state of perfect division to the oxygen of the air. Lastly, M. Therault is of opinion that oil of valerian is not a substance of a complex nature, and that it may be entirely converted into valerianic acid.

This conversion is readily explained. According to Ettling, the formula of valerianic acid is  $C^{20} H^{18} O^3 + H_2 O$ ; if that of oil of valerian be  $C^{20} H^{20} O^2$ , and if two atoms of oxygen be made to intervene, one of which combines with two atoms of hydrogen to form water, and the other be added, we shall have the following equation :



M. Therault finishes his memoir with observing, that the process for extracting valerianic acid, proposed by Messrs. Smith of Edinburgh in the *Journal de Pharmacie* for January last, appears to be a good one; excepting that he would propose to use a caustic instead of a carbonated alkali, and after having boiled the mixture, to expose it for a month to the air, stirring it several times a day; not to subject the residue to pressure, and to distil with the roots, which greatly facilitate the operation. When afterwards the distilled liquor has been saturated by means of an alkali, and the valerianate of potash or soda has been concentrated, it is essential not to employ an excess of sulphuric acid to separate the valerianic acid; it would be better to leave a small portion of the valerianate undecomposed, for towards the end of the distillation, the organic matter mixed with the salt is carbonized and sulphurous acid is formed, which appears to react upon the valerianic acid.—*Journ. de Pharm. et de Ch.*, Septembre 1847.

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**NOTE ON THE MEASUREMENT OF THE DOUBLE SULPHATES OF ZINC AND SODA, AND OF MAGNESIA AND SODA. BY PROF. W. H. MILLER.**

The crystals were not good enough for me to obtain a very satisfactory result from a few observations; they are however sufficiently good to show that they are isomorphous.

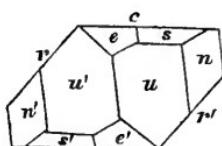
The crystals belong to the oblique prismatic system.

The angles between normals to the faces are—for the oxide of zinc salt,

$$\begin{array}{lll} n\ n' & 113^\circ & 4 \\ u\ u' & 74^\circ & 12 \end{array}$$

the angle between a normal to  $c$  and the intersection of

$$\begin{array}{ll} u, u' = 10^\circ 22' \\ u\ c & 83^\circ 46' \\ r\ c & 49^\circ 54' \end{array}$$



The symbols of the simple forms, in the notation which I use, are—

$$\begin{array}{lll} c\ 001, & r\ \bar{1}01, & n\ 110, \\ u\ 120, & e\ 011, & s\ 121. \end{array}$$

The faces of the magnesian salt are more irregular than those of the former, so that I cannot pretend to determine the difference between the angles of these crystals.

The angles given above must be considered as rough approximations only. In a little time perhaps I may be able to obtain more accurate values of them.—*From the Proceedings of the Chemical Society*, vol. iii. p. 391.

#### NATIVE CARBONATE OF NICKEL.

This new mineral was exhibited last year at the Philosophical Society's exhibition in Glasgow, and was examined at the time, at the request of Dr. R. D. Thomson, by his pupil Mr. John Brown, in the College Laboratory. It occurs in the form of thin green crystalline layers, on the surface of chrome iron ore from America. It dissolves with effervescence in dilute hydrochloric acid. The solution is precipitated black by sulphohydret of ammonia; is precipitated and dissolved in excess by caustic ammonia, yielding a characteristic coloured solution. Caustic soda precipitates the solution green, without resolution. It is accompanied, apparently in union, by carbonates of lime and magnesia—isomorphous bodies. The fact of its occurring on the surface of chrome iron, and having been mistaken for sesquioxide of chrome, renders it probable that oxide of nickel may exist in that mineral occasionally.—R. D. T.

#### AN EXAMINATION AND ANALYSIS OF THE "NADELERZ," OR NEEDLE ORE OF BISMUTH. BY E. J. CHAPMAN, ESQ.

THE "needle ore" occurs in thin prismatic crystals, generally forming more or less radiated groups imbedded in quartz, at Ekatherinenburg in Siberia, the only known locality in which it has been hitherto found. The crystals are too imperfect to admit of measurement; but they appear to belong to the Trimetric or Prismatic system, and to have for the primary form a right rectangular prism, or perhaps more correctly a right rhombic one, in which the angle MM closely approaches a right angle.

The colour of this mineral is dark steel-gray on the fractured surface, but externally the true colour is usually masked by a yellow tarnish. The powder or "streak" is black; the degree of hardness 2·0 to 2·5, or between that of rock-salt and calc-spar; and the specific gravity about 6·1.

Before the blowpipe it fuses instantly and may be almost entirely volatilized, forming a yellow incrustation of the mingled oxides of lead and bismuth on the support. The presence of bismuth and copper may be ascertained by fusion with "microcosmic salt" and a little tin on charcoal in the reducing flame, when the lead, which is clear whilst hot, becomes on cooling of a grayish-black colour with red patches. With carbonate of soda on charcoal in the same flame, it forms an alkaline sulphuret. The lead is best detected by boiling a fragment in nitric acid, filtering, dissolving the residue (sulphate of lead) in caustic potash, diluting the solution, and reprecipitating by sulphuric acid.

This ore was first described by Karsten and analysed by John; and although a considerable period has elapsed since the date of this analysis, yet, probably from the rarity of the mineral, its composition

has been examined by but one other chemist, Frick, in Poggendorff's 'Annalen,' xxxi. p. 529.

These analyses have given—

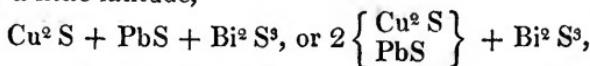
1. By John :—

	Per cent.	Atomic relations.	
Sulphur.....	11·58	0·057	3
Bismuth .....	43·20	0·032	2
Lead.....	24·32	0·018	1
Copper.....	12·10	0·031	2
Nickel .....	1·58		
Tellurium.....	1·32		
Gold.....	0·79		
		94·89	

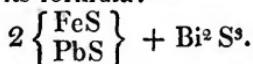
2. By Frick :—

Sulphur .....	16·61	0·0826	6
Bismuth .....	36·45	0·0410	3
Lead .....	36·05	0·0270	2
Copper .....	10·59	0·0267	2
	99·70		

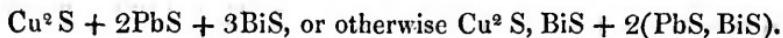
The first analysis does not admit of any rational formula; but if we consider the loss, more than 5 per cent., to be sulphur, we may obtain by a little latitude,



a formula analogous to that of the kobellite from Ilvena in Sweden, analysed and named by Setterberg, and in which the electro-negative atoms in the base are to the electro-negative atoms in the acid as 2 to 3. The following is its formula :—



The second analysis yields also but an inexpressive and unsatisfactory result. The formula, if such it can be termed, obtained from it is—



I have now to enter into the details of a third analysis, executed lately by myself, on a specimen kindly given to me by Colonel Jackson, F.R.S., who brought it with him from Russia. The ore was accompanied in the quartz by minute tufts of malachite, which, together with the matrix, were carefully removed, by the aid of a microscope, from the substance analysed.

8·38 grs. of the mineral in powder were boiled in strong nitric acid.

A residue of 4·92 grs. of sulphate of lead remained, and 0·26 grs. of sulphur. The 4·92 grs. of sulphate of lead (obtained, it should be stated, after solution of the residue in potash and subsequent re-conversion) = 3·36 grs. of lead and 0·52 of sulphur.

Carbonate of ammonia in excess was then added to the clear solution; and after remaining for three hours at a gentle heat, it was filtered from the precipitate, which (after being well-washed with

the same reagent, and the "washings" added to the original solution) was dissolved in acetic acid; and a slip of pure lead being immersed in the solution, the whole was covered up immediately and suffered to stand for four hours. The slip of lead weighed 22·63 grs.

The four hours having elapsed, the lead was taken from the solution, and, after separation of the precipitated bismuth, dried and weighed. It weighed 19·21 grs.; loss, 3·42 grs. On the addition of sulphuric acid, 5·03 grs. of sulphate of lead were obtained, which are equal to 3·435 of lead; and this amount corresponding so nearly with the loss in the metallic precipitant, the whole of the lead present in the mineral may be considered to have been converted into  $PbO, SO_3$  by the first operation.

The bismuth precipitate was washed with cold distilled water (which had been boiled), dissolved in nitric acid, and again thrown down by carbonate of ammonia. The oxide of bismuth weighed 2·60 grs., equivalent to 2·33 grs. of bismuth.

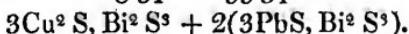
To the original solution (containing carbonate of ammonia) a few drops of ammonia were added, and it was then gently evaporated until the ammoniacal odour was entirely destroyed. Solution of potash was then added, and the whole boiled. The black oxide of copper, well-washed with hot water, ignited, and weighed in a covered crucible, came to 1·31 grs., an amount equal to 1·05 of copper.

Finally, chloride of barium was added to the potash solution, which produced a precipitate of sulphate of baryta weighing 5·72 grs., an amount corresponding to 0·79 of sulphur. The whole of the sulphur present in the mineral was therefore

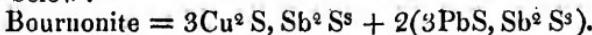
$$1\cdot57 \text{ grs. } (0\cdot52 + 0\cdot26 + 0\cdot79).$$

The following table exhibits the above analysis and its atomic deductions:—

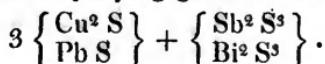
		Per cent.	Atomic relations.
Sulphur .....	1·57	18·78	0·0935    3 or 18
Bismuth .....	2·33	27·93	0·0315    1 or 6
Lead.....	3·36	40·10	0·0309    1 or 6
Copper.....	<u>1·05</u>	<u>12·53</u>	0·0317    1 or 6
	8·31	99·34	



This formula is identical with that of the bournonite (from the analyses of H. Rose, Smithson, &c.), substituting only  $Bi^2S^3$  for  $Sb^2S^3$ , as below:—



In each ore, the electro-negative atoms in the basic compounds are, to the electro-negative atoms in the acid compounds, as 1 to 1, as expressed in the accompanying general formula:—



As the bournonite crystallizes also in the same system as the needle ore, and indeed affects probably the same primary form within close measurements, the isomorphous relationship of these minerals is sufficiently apparent.

Most English mineralogists give a right rectangular prism for the primary form of the bournonite; but Dufrénoy, in his recent Treatise, vol. iii. p. 18, after an examination of numerous crystals, considers a right rhombic prism in which the angle MM =  $93^{\circ} 40'$  to be the correct primary form. The modified rectangular prism in which the bournonite usually occurs is in this light a secondary form, derived from the primary by the replacement of its lateral edges by the planes  $g' h'$  in the notation of Hauy.

The specimen of the needle ore which furnished the above analysis, exhibited here and there in the quartz transverse rhombic sections, in which an accustomed eye might easily perceive that the obtuse angle was included between  $90^{\circ}$  and  $100^{\circ}$ .

I could not detect in this specimen the presence of tellurium, found by John in the needle ore; it is however perfectly conceivable that, under certain circumstances, a portion of the PbS may be replaced by PbTe.—*From the Chemical Gazette for September 1, 1847.*

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#### ACTION OF ANHYDROUS PHOSPHORIC ACID ON AMMONIACAL SALTS. BY M. DUMAS.

The author finds that when anhydrous phosphoric acid is made to react upon crystallized acetate of ammonia, there distils a liquid the fixed boiling-point of which is  $170^{\circ}$  F., and which is miscible with water in all proportions. When purified by digestion with a saturated solution of chloride of calcium, and then distilled from solid chloride of calcium and from magnesia, it still possesses the boiling-point above mentioned.

Analysis gave the following numbers:—

	Experiment.	Calculation.
Carbon .....	57·4	58·5
Hydrogen.....	7·4	7·3
Nitrogen .....	34·4	34·2
	99·2	100·0

The density of the vapour gave the number 1·45. The above results lead to the very simple formula  $C^4 H^3 N$ , which differs from acetate of ammonia by four equivalents less of water. Its composition is similar to that of nitroguret of acetylene.

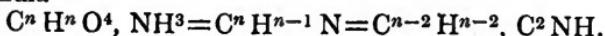
But a point of view, which the reactions will warrant, would give to this substance the following rational formula,  $C^2 NH$ ,  $C^2 H^2$ , which would make hydrocyanate of methylene of it, or an isomeric of it.

The reactions which have been examined gave rise to some curious phenomena. Thus solution of potash at a boiling heat disengages ammonia and regenerates acetic acid; chromic acid has no action; nitric acid is not decomposed by this liquid even when heated to ebullition. Potassium acts vividly in the cold, and with the disengagement of heat; cyanide of potassium is formed, and an inflammable mixture of free and carburetted hydrogen gases is evolved.

It is well known that M. Fehling obtained a substance of analogous composition to that now described by distilling benzoate of ammonia with a naked fire: he did not however attach to the discovery the views which have been now developed, nor did he study

its reactions. M. Dumas proposes to examine, under the new point of view described, the action of anhydrous phosphoric acid on the ammoniacal salts formed by the volatile organic acids.

M. Dumas remarks that if the product which he has obtained should constitute a compound identical with hydrocyanate of methylene, all these ammoniacal salts, treated in the same manner, should yield æthers corresponding to certain alcohols, according to the general formula—



In decomposing the latter by potash, there might be produced alcohol  $\text{C}^{n-2} \text{H}^{n-2}$ ,  $2\text{HO}$ , and prepared by this method, all the alcohols from the fatty acids.—*Comptes Rendus*, Septembre 13, 1847.

#### METEOROLOGICAL OBSERVATIONS FOR OCT. 1847.

*Chiswick*.—October 1. Hazy: cloudy. 2. Cloudy. 3. Light clouds and fine: overcast. 4. Foggy: fine. 5. Fine: light clouds: clear at night. 6. Dense fog: very fine: lightning and rain at night. 7. Fine: rain: lightning at night: clear. 8. Very fine. 9, 10. Rain. 11. Rain in forenoon: clear at night. 12. Slight fog: very fine. 13. Foggy: hazy: cloudy at night. 14. Hazy and drizzly: cloudy. 15. Hazy and cold: slight rain. 16. Foggy: very fine. 17. Foggy, with slight drizzle: very fine. 18. Slight fog: rain. 19. Exceedingly fine: rain. 20. Very fine: rain at night. 21. Rain: clear at night. 22. Fine. 23. Densely clouded and boisterous: rain. 24. Slight showers. 25. Very clear: fine: clear and frosty. 26. Frosty: uniformly overcast. 27. Fine: rain. 28. Hazy and mild. 29. Exceedingly fine. 30. Overcast and mild. 31. Cloudy and mild.

Mean temperature of the month .....	52°.14
Mean temperature of Oct. 1846 .....	50°.37
Mean temperature of Oct. for the last twenty years .....	50°.42
Average amount of rain in Oct. ....	2.60 inches.

*Boston*.—Oct. 1—5. Cloudy. 6. Rain. 7. Fine: rain p.m. 8. Fine. 9. Fog: eclipse of the sun invisible until three-quarters over: fog. 10. Rain: rain a.m. 11—13. Fine. 14, 15. Cloudy. 16. Fine. 17, 18. Fog. 19, 20. Fine. 21. Cloudy: rain a.m. 22. Fine. 23. Cloudy: rain p.m. 24—26. Fine. 27. Rain: rain a.m. and p.m. 28. Fog. 29. Rain: rain a.m. 30. Fine: rain a.m. 31. Cloudy.

*Sandwick Manse, Orkney*.—Oct. 1. Clear: cloudy. 2. Cloudy: clear. 3. Cloudy. 4. Cloudy: drops. 5. Bright: showers. 6. Showers. 7. Drizzle. 8. Drizzle: clear: aurora. 9. Clear: cloudy. 10. Cloudy: drizzle. 11. Clear: fog. 12. Fog. 13. Cloudy: clear: aurora. 14. Cloudy: clear. 15, 16. Clear: cloudy. 17. Showers: drizzle. 18. Rain. 19. Damp: rain. 20, 21. Showers: clear. 22. Showers: rain. 23. Showers: sleet-showers. 24. Sleet-showers. 25. Clear. 26. Drops: showers. 27. Bright: drops. 28. Cloudy. 29. Cloudy: shower: lightning. 30. Showers: rain. 31. Bright: cloudy.

*Applegarth Manse, Dumfries-shire*.—Oct. 1, 2. Chill and droughty. 3, 4. Dull, but fair. 5. Fair a.m.: showery p.m. 6. Heavy rain a.m. 7. Heavy rain a.m.: flood. 8. Frequent showers. 9. Fine a.m.: rain p.m. 10. Heavy rain. 11. Fair: rain in the night preceding. 12. Fair and fine. 13. Fair, but raw and cloudy. 14, 15. Fair, though chilly. 16. Very fine clear day. 17. Dull and cloudy. 18. Dull and cloudy: rain p.m. 19. Heavy rain. 20, 21. Occasional showers. 22. Rain a.m.: very heavy p.m. 23. Rain early a.m.: fine day. 24. Heavy showers. 25. Fair: fine: clear. 26. Rain nearly all day. 27. Heavy rain and flood. 28. Fog: cleared p.m. 29. Fair and fine. 30. Fair a.m.: heavy rain p.m. 31. Rain early a.m.: cleared.

Mean temperature of the month .....	49°.5
Mean temperature of Oct. 1846 .....	49°.5
Mean temperature of Oct. for twenty-five years .....	49°.6
Average rain in Oct. for twenty years .....	3.56 inches.
Rain in Oct. 1847 .....	5.09 "

*Meteorological Observations made by Mr. Thompson at the Garden of the Horticultural Society at Chiswick, near London; by Mr. Veall, at Boston; by the Rev. W. Dunbar, at Applegarth Manse, Dumfries-shire; and by the Rev. C. Clouston, at Sandwick Manse, Orkney.*

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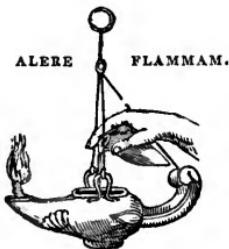
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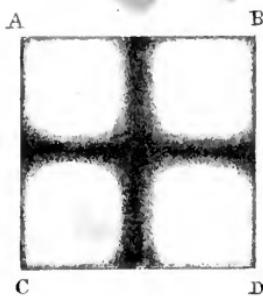
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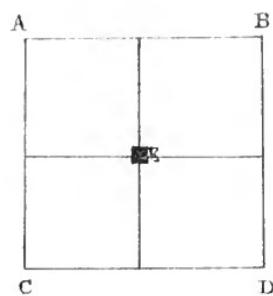
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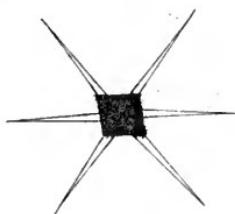
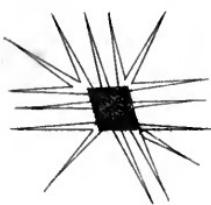
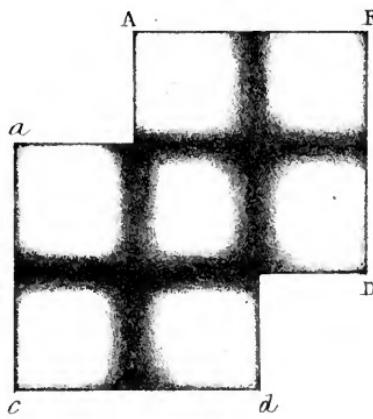
**FIG. 1.**



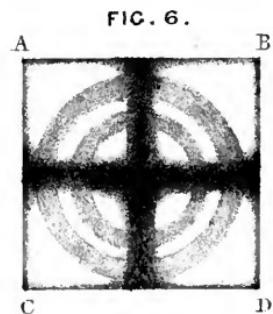
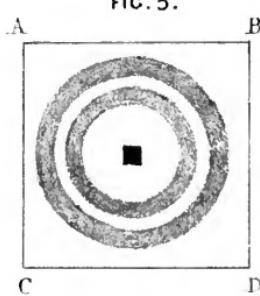
**FIG. 2.**



**FIG. 3.**



**FIG. 4.**





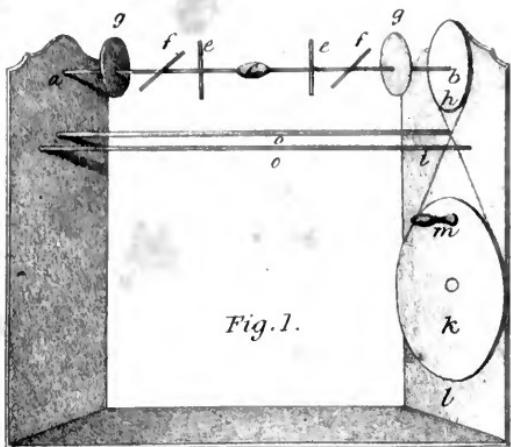


Fig. 1.

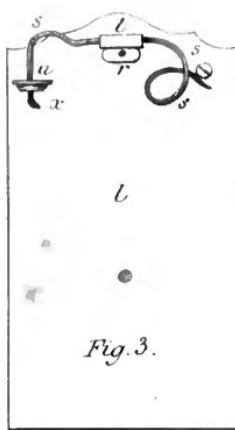


Fig. 3.

Fig. 2.



Fig. 2.

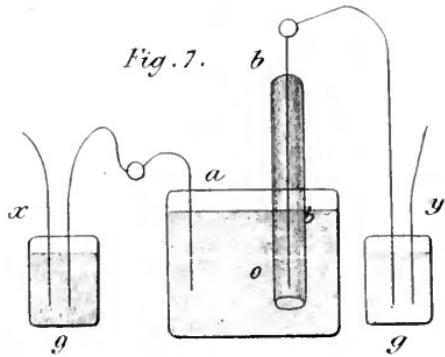


Fig. 4.

Fig. 5

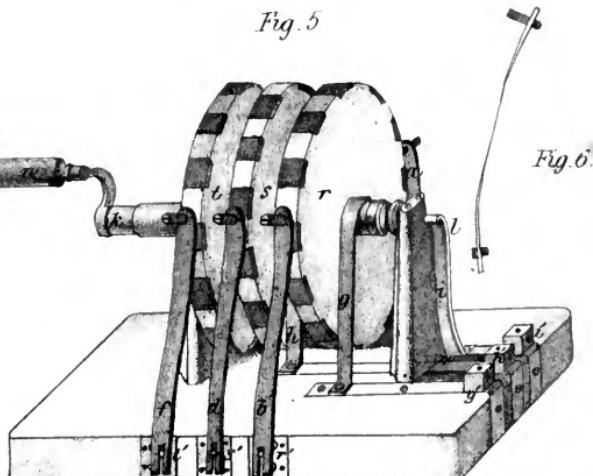
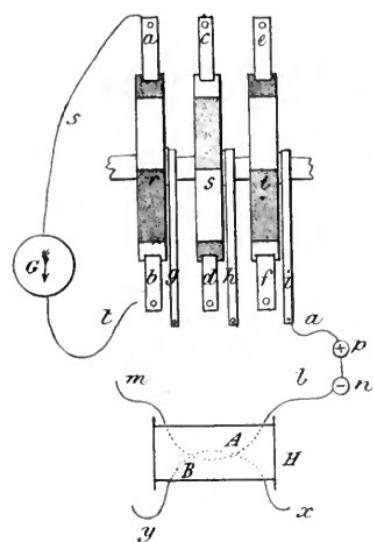
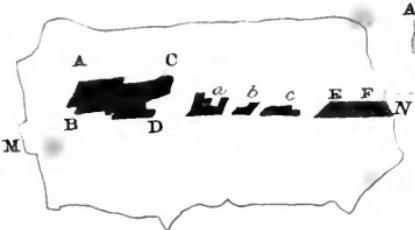


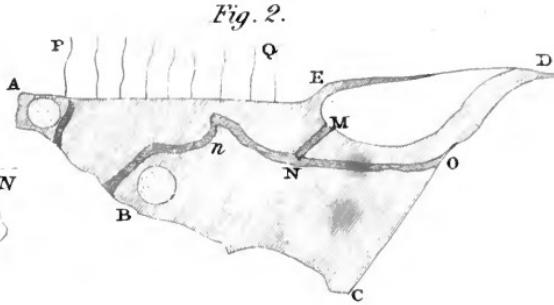
Fig. 6.



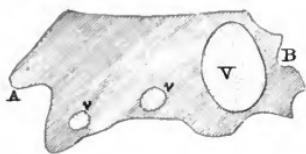
*Fig. 1.*



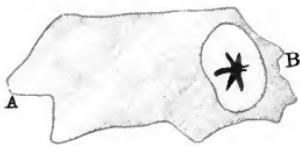
*Fig. 2.*



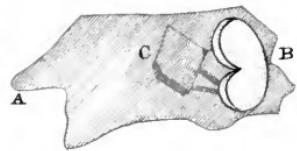
*Fig. 3.*



*Fig. 4.*



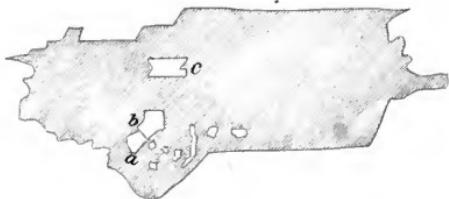
*Fig. 5.*



*Fig. 6.*



*Fig. 7.*



*Fig. 8.*

